AO-A019 108

EVALUATION OF ADDITIVES TO REDUCE SOLID PROPELLANT
FLAMMABILITY IN AMBIENT AIR

Leonard H. Caveny, et al

Princeton University

Prepared for:

Ballistic Research Laboratories

Oecember 1975

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CONTRACT REPORT NO. 278

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Princeton University
Princeton, New Jersey

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER CONTRACT REPORT NO. 278	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) EVALUATION OF ADDITIVES TO REDUCE SOLID PROPELLANT FLAMMABILITY IN AMBIENT AIR		5. TYPE OF REPORT & PERIOD COVERED Technical 1 Dec 1971 - 30 Nov 1974
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Leonard H. Caveny, Anthony Z. Mackiewicz and Martin Summerfield		8. CONTRACT OR GRANT NUMBER(s) DAAD05-72-C-0135
9. PERFORMING ORGANIZATION NAME AND ADDRESS Princeton University Princeton, N.J.		10. PROGRAM ELEMENT. PROJECT, TASK AREA & WORK UNIT NUMBERS 1J662604AH97
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Ballistic Research Laboratories Aberdeen Proving Ground, MD		12. REPORT DATE DECEMBER 1975
		13. NUMBER OF PAGES 91
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) US Army Materiel Command 5001 Eisenhower Avenue Alexandria, VA 22333		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

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JAN 12 1976

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Solid propellants,   Flame retardants,
Flammability,   Hazard reduction.
Extinguishment,
Ignition,

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An experimental investigation to obtain an understanding of how chemical additives (i.e., flame inhibitors, char formers, and coolants) intended to reduce the likelihood of accidental ignition and flammability affect the combustion of high energy propellants in ambient air. Several composite propellants were made more resistant to ignition. However, test results for high energy propellants revealed that (once ignition occurred) the continual resupply of reactants (both air and propellant products) overwhelms the contributions of

20. Abstract - continued

the additives and prevents self-extinguishment in ambient air. In some cases
elimination of the conventional external flame resulted in smoldering which
produced extremely hazardous, explosive gases. The investigation revealed
the following encouraging trends. Several low energy materials (i.e., impetus
less than 200,000 ft-lb/lb) suitable for outer-layer protective coatings
appear to be promising with respect to their ability to self-extinguish and
to be resistant to ignition under ambient conditions. Several of the
moderately high energy nitramine composite propellants with high decomposi-
tion temperature binders are several times more resistant to accidental
ignition than conventional propellants and are easily extinguished, if
ignited.

FOREWORD

The Technical Monitor for this program was Dr. A. W. Barrows of the Ballistic Research Laboratories. During the course of the study the following individuals were particularly cooperative in arranging for test specimens and providing advice: M. Visnov, Frankford Arsenal; E. Costa, Picatinny Arsenal; R. Reed, J. A. Peterson, and E. Lawton, Wasatch Division, Thiokol Corp.; R. A. Biddle, Elkton Division, Thiokol Corp.; G. A. Lo, Rocketdyne Division, Rockwell International; C. N. Bernstein, Small Arms System Agency; and A. A. Juhasz and J. J. Rocchio of the Ballistic Research Laboratories. The concept of a high ignition temperature/self-extinguishing propellant (HIT/SEAP) under ambient conditions was defined by L. Ambrosini while he was Director of the Small Arms System Agency.

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I. INTRODUCTION

This report summarizes an investigation of chemical means of reducing the flammability and the likelihood of accidental ignition of solid propellants in ambient air. The overall goal of the investigation was to develop an improved understanding of the mechanisms by which flame retarding additives could reduce flammability (in ambient air). The scope of the total study and the criteria for successfully reducing flammability are given in an earlier report.*[1] The results of the investigation have utility in rationalizing the choice of propellant formulations, charge configuration, process techniques, and special additives to reduce flammability.

This report, along with a previous report,[1] were part of a broadly based U.S. Army effort to develop high energy propellants to meet the following requirements:

> The propellant shall resist ignition, shall self-extinguish following removal of the ignition stimulus, shall have good ballistic and physical properties, and shall burn readily at elevated pressures in combustion chamber conditions.

The desired characteristics of these propellants have been summarized by the designation HIT/SEAP, i.e., high ignition temperature/self-extinguishing at atmospheric pressure.

In the studies at Princeton University, the emphasis was on understanding the combustion processes and not on developing propellants. Several organizations and laboratories were given contracts specifically aimed at developing propellants resistant to accidental ignition and to sustained combustion under atmospheric conditions.[2-6]

Propellants burning in ambient air are depicted in Fig. 1, which shows the interaction between the combustion products which evolve at the burning surface and the ambient air. When burning is vigorous and the momentum of the gases leaving the burning surface is relatively high, the diffusion flame between the products of the self-flame and the ambient air is only loosely coupled to the reactions at the propellant surface

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*For continuity and completeness purposes, there is a slight overlap between this report and Ref. 1.

(see Fig. 1a). In that case, even though the reactions with air greatly increase the flame temperature, the diffusion flame is too far from the surface to increase greatly the temperature gradient at the surface. Modifications which reduce the propellant burning rate (under ambient conditions) also reduce the blowing rate at the surface and, thereby, permit the propellant products/air diffusion flame to move arbitrarily close to the reacting surface. Indeed, as shown in Fig. 1b, when the burning rate is sufficiently low, oxygen in the ambient air diffuses through the flame zone to the propellant surface and accelerates the surface reactions. Figure 1b illustrates a very important realization in the search for low flammability propellants, i.e., the very modifications that tend to decrease the intensity of the self-flame increase the relative heat feedback contribution of the propellant products/air diffusion flame.

Figure 2 illustrates schematically the self-extinguishment requirement that is desired of low flammability propellants. The sketches show the pressure and temperature domain in which the propellants are intended to operate along with the boundary for self-extinguishment, following removal of the ignition stimulus. The upper sketch represents the situation of all of the conventional high energy propellants which are in use presently, i.e., the propellant will not self-extinguish within the major portion of the operating domain. The lower sketch shows the desired situation of a propellant whose boundary for self-extinguishment is totally above the pressure and temperature domain. As indicated in the sketches, increasing pressure and temperature makes self-extinguishment less likely. Accordingly, throughout this report interest is focused on propellant modifications which tend to shift the self-extinguishment boundary to the higher ambient pressures and temperatures.

II. CHEMICAL APPROACHES TO REDUCING FLAMMABILITY

The reduction of flammability achieved by adding flame retardants has numerous practical and commercial applications. In the case of textiles and plastics, an extensive technology has been developed through which a wide range of chemically distinct additives can be utilized to retard flammability while other desirable properties are retained.[7] There is broad experience on which to relate retardant characteristics such as elemental composition, chemical structure, and degree of loading to the reduction of flammability. While the successes of applied chemistry in flame retardance are clearly apparent, it has become increasingly important, as requirements for reducing the flammability of combustible materials become more stringent, to develop a better understanding of the mechanisms by which flame retardants function.

The initial efforts to reduce the flammability of propellants have centered on approaches that have been applied successfully to reduce the flammability of plastics and polymers.[7] From that experimental data base, the following have been shown to be useful and practical: (1) flame inhibitors (additives containing halogen atoms) which decompose to yield species which suppress the gas phase reactions near the burning surface, (2) compounds which promote the formation of carbonaceous surface layers that block heat feedback from the flame and the diffusion of atmospheric oxygen to the surface, and (3) coolants which absorb large amounts of energy near the burning surface.

It is recognized that the inhibition of flames can more effectively be achieved by chemical rather than physical means. However in practical fire retardance situations, both physical and chemical constraints operate. For example, advances in flammability reduction can be negated if the propellant is subjected to extreme heating conditions or to unusual convective burning situations.

A. Flame Retardants

A hypothesized flame retardant mechanism for halogen compounds is flame inhibition action by means of radical trapping in the vapor phase.[7] The additive decomposes near the burning surface and forms free radicals

in the flame. Oxidation in the vapor phase is a process involving free radicals, e.g., H·, OH·, O·, and HO_2·. The flame retarding action of the halogen additive is attributed to the ability of the added substance to trap these radicals. Reactions of bromine compounds are a good example of this;

$$RBr + H· \rightarrow HBr + R·$$

For flame inhibition to occur, the generated species R· must be a less active radical than H· which is to be removed. In general, H·, OH·, and the like, will be the most active species and their removal should greatly retard the flame zone reactions.

In a hydrocarbon/air flame, halogens act as acceptors of free radicals and as inhibitors of combustion of CO. The most important reactions are probably:

$$OH· + CO \rightarrow CO_2 + H· \qquad \text{(A) exothermic}$$
$$H· + O_2 \rightarrow OH· + O· \qquad \text{(B) chain branching}$$

Hydrogen is formed in reaction (A) and used in reaction (B). The OH· radical is formed in reaction (B) and used in reaction (A). A chain reaction is thereby initiated; attempts can be made to interrupt it by reducing the concentration of H· and OH·. Halogens, especially bromine, can play a part in this interruption. Hydrobromic acid, from bromine compounds, interacts with the highly reactive OH· radical and give rise to the following reactions:

$$OH· + HBr \rightarrow H_2O + Br· \qquad \text{(C) inhibition}$$
$$Br· + RH \rightarrow HBr + R· \qquad \text{(D) regeneration}$$

RH is an organic compound containing hydrogen. The practical result is that OH· is replaced by a less active species Br· or R· and the chain reaction ceases as a consequence. Since the bond strength of HBr is less than that of HCl (86 vs 102 kcal/mole) reaction (C) would progress more slowly with HCl. This observation explains why bromine is usually a more effective flame retardant than chlorine, a fact which is clearly confirmed by fire retardants added to commercial plastics.

To be an effective flame retardant in a propellant formulations, the halogen additive must be added as a solid and decompose at the burning surface. Experience has shown that liquid additives cannot be easily

-4-

rstainad in the propellant. Particular attantion must be given to insure that solid additives decompose readily at tha surface to form the active spsciaa necessary for flame inhibition. Tha structure of tha additive influences the ease with which it decomposas and the species it yields. An affactive flame inhibitor most likaly will havs its predominant affect in the thin flame zona near the burning surfaca of ths propellant where the reactive species can ba neutralized more affectively.

B. Char Formers

Savaral phosphorus containing compounds have baen idantified as pro-moting char layers.[7] As the parent matarial burns, these phosphorus com-rounds react to yield long chain carbon compounds and eventually a char layer. As this char layer davalops, one hypothesis (illustratad in Fig. 3) is that it partially insulates tha surface from haat feedback from the flame and isolates the surfaca reaction zone from atmospheric oxygen. After the ignition stimulus is removed and the burning rate adjusts, flame inhibition stretches out the self-flame. During the early stages of burning, the char laysr begins to insulate the surface from the diffusion flame. If char formation is successful as a fire retardant, heat faedback from tne air/propellant products flame to the propellant surface should become progressively wsaker until the affacts of ambient air become un-important (Fig. 3c).

It is known that most organo-phosphorus compounds are effective flame retardants while non-volatile phosphorus salts of metals are not. Tha phosphorus compounds tand to create mora char and less flammable volatilas. Ths important element is the production of an acid that is difficult to volatize. Substancas that give rise to acid fragments on heating appsar to havs the desired affect when usad in commercial plastics. Phosphoric acid has a high boiling point (130 - 200 C) and therefore remains in the solid or liquid phases sufficiantly long to function as a char former. Indeed, aftar burning a substance treated with a phosphor-us compound, a sticky viscous liquid is usually found which is polymeric acid containing phosphorus.

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A specific mechanism for char formation has not been well established and investigators have postulated mechanisms that differ depending upon the parent material and the phosphorus compound added. One particular mechanism of char formation suggests an initial decomposition of the parent material and molecular rearrangements catalyzed by acids. The initial decomposition products must then decompose to volatile fragments or react further to produce char. The char presumably is highly cross-linked and reduced to almost pure carbon.

Phosphorus can have several oxidation states varying from +5 to -3 and there seems to be some relation between fire retardance and the phosphorus oxidation state. The stability of organo-phosphorus compounds increases from phosphates and phosphites to phosphonates to phosphine oxide.

The phosphorus additive may react with the propellant binder during the curing process or at the burning surface. Processing of the polymer with nitrogen compounds has shown that the esterification reaction of the phosphate compound with the hydroxyl group of the binder takes place smoothly and rapidly.[7]

$$R-OH + HO-\overset{\overset{O}{\|}}{P}-(OH)_2 + (NH_2)_2CO \rightarrow R-O-\overset{\overset{O}{\|}}{P}-(OH)_2 + 2NH_3 + CO_2$$
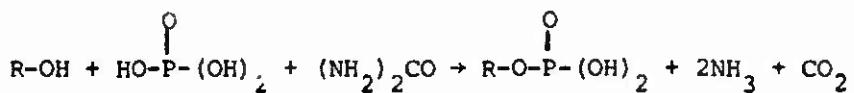
where R is some molecule with an available hydroxyl group, e.g., cellulose. The urea probably functions as a dehydrating agent promoting the phosphorylation of the hydroxy-material.

Consider the PBAA-EPON system that serves as the binder in some composite propellants,

Cure Reaction of PBAA-EPON System

Epoxy-Carbonyl Bond   Hydroxyl group
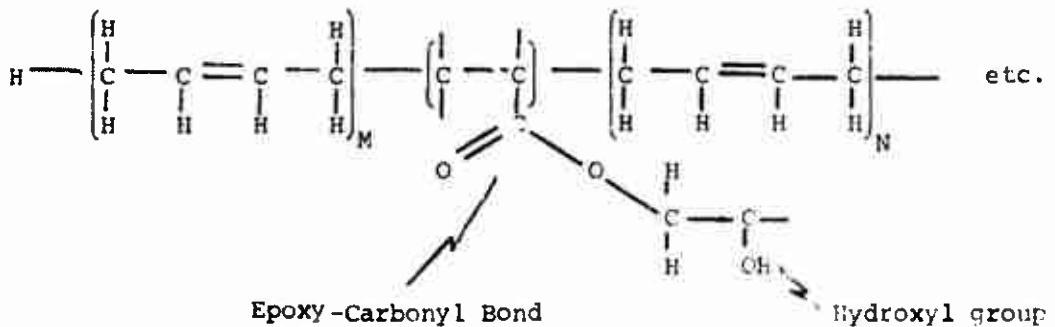
where M and N indicate repeating units.

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Phosphorylation of the binder probably takes place at a hydroxyl group from the epoxide added as the curing agent in the cure reaction. The extent of phosphorylation will depend upon the number of available hydroxyl groups in the propellant binder.

Phosphorus additives also function through free radical reactions with propellant decomposition products. Probable reactions leading to inhibition in flames containing phosphorus are as follows;[7]

$$R_3PO \rightarrow PO\cdot, P\cdot, \text{and } P_2$$

$$H\cdot + PO\cdot + M \rightarrow HPO\cdot + M$$

$$OH\cdot + PO\cdot \rightarrow HPO\cdot + O\cdot$$

$$HPO\cdot + H\cdot \rightarrow H_2 + PO\cdot$$

where M is some third body (nonreactive molecule)
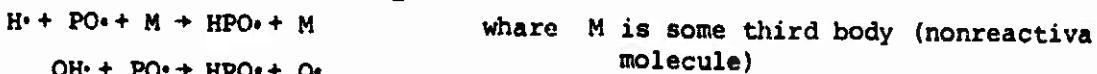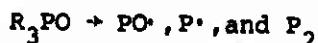
Other likely reactions are;

$$P_2 + O\cdot \rightarrow P\cdot + PO\cdot$$

$$P\cdot + OH\cdot \rightarrow PO + H\cdot$$
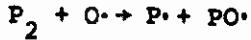
In H atom recombination reactions, the main species are P_2, $PO\cdot$, and $PO_2^\cdot$ with lesser amounts of $P\cdot$, $HPO\cdot$, and PN. The species $HPO\cdot$ is readily observed in flames by its characteristic green chemiluminescence. An additional affect by the phosphorus compounds considers the formation of free radicals which may act as flame inhibitors in a manner similar to that of the halogen additives.

C. Coolants

To realize fully the flammability reducing capacity of a particulate coolant added to a propellant, the coolant must endothermically decompose before it leaves the surface of the matrix propellant. The following are examples of compounds which can be considered as coolants when added to propellants:

Oxamide $C_2H_4N_2O_2$ $M_w = 88$

$$NH_2 - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} - NH_2$$

Ammonium Oxalate $C_2H_8N_2O_4$ $M_w = 124$

$$NH_4O - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} - ONH_4$$

Hydroxylammonium Oxalate $C_2H_8N_2O_6$ $M_w = 166$

$$HOH_3NO - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} - ONH_3OH$$
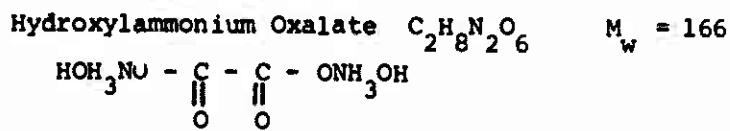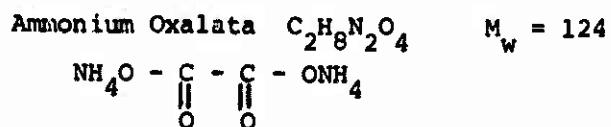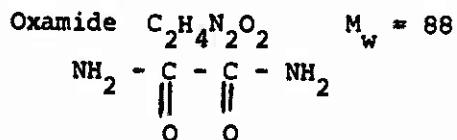
Figure 4 illustrates two situations: (a) the undesirable situation of a coolant decomposing after it leaves the propellant surface, and (b) the desirable situation of a coolant endothermically decomposing at the propellant surface. The difference between the surface temperatures of the matrix propellant and the decomposition of the coolant is the important consideration in terms of the above premise. The temperature of decomposition at slow heating rates is a secondary consideration since the low temperature decompositions that occur during slow heating are not indicative of the higher condensed phase temperatures that accompany rapid ignition and self-sustaining combustion. As the coolant decomposes endothermically it may lower the temperature of the flame, or in addition, it may evolve large volumes of slow reacting gases which dilute the oxygen supply near the burning surface of the propellant. Small particles formed from the decomposition of the coolant may also inhibit the flame.[8,9]

Two of the proposed mechanisms by which coolants retard flame are summarized as follows. The first relies on a heterogeneous mechanism such as radical recombination on a particle surface,

$$R\cdot + M \rightarrow RM \qquad\qquad RM + R'\cdot \rightarrow RR' + M$$

where M is the colliding solid and the inhibitor and R· (the reactive species and chain carrier) is temporarily adsorbed on the surface of M and is prepared for easy reaction with another radical R'·, the excess of the liberated energy being transferred to the inhibitor M. Thus, M acts as a coolant. The second relies on a homogeneous mechanism involving at least partial volatilization of the small particles, producing some gaseous inhibiting species such as K, K^+, or KOH which react with the active chain species. It is proposed that the gaseous KOH removes H and OH radicals via

$$KOH + H\cdot \rightarrow H_2O + K \qquad \text{and} \qquad KOH + OH\cdot \rightarrow H_2O + KO.$$
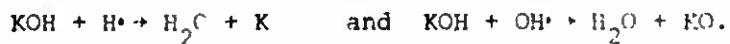
Volatile alkali metal salts acting as coolants may be effective in reducing flammability[9,10] Their effectiveness depends on

(1) the increase in surface area accompanying the reaction,

$$Solid(I) \rightarrow Solid(II) + gas \qquad\qquad and$$
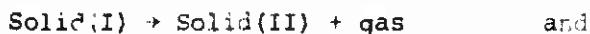
(2) the particle size and burning rates which determine a residence time in the flame sufficient to allow the decomposition of the original solid within the flame front.

Inhibition is considered to occur via a homogeneous mechanism, involving the volatilization and/or reaction of the initially formed submicron particles to provide gaseous hydroxide as the inhibiting species. In order that the generation of aklali oxide or hydroxide may be facilitated, the anion associated with the alkali metal ehould be of low acid strength (i.e., oxide, carbonate, chloride, and phosphate). The effectiveness of the coolant depends upon the ability of the alkali salt to pyrolyze to give the alkali hydroxide and the resulting removal of chain branching radicals.

III. EXPERIMENTS FOR MEASURING COMBUSTION CHARACTERISTICS

In this report, references will be made to four types of experiments which were used to measure the effectiveness of flammability-reducing modifications. These experiments as illustrated in Fig. 5 are: (1) forced convection using a calibrated acetylene flame (shown in Fig. 6), (2) conductive heating using an electrically heated copper plate (experiments carried out at BRL[11]), (3) radiation using a quartz/tungsten lamp (heat flux up to 10 cal/sec-cm^2), and (4) sustained burning in a controlled atmosphere.

A. Regulated Atmosphere

As part of this study a combustion chamber for conducting experiments under a range of atmospheric conditions was developed. Figure 7 shows the chamber arranged for photographic measurements. The features of the combustion chamber and its associated equipment include:

(1) Pressure can be regulated from 1.0 atm to 0.05 atm.

(2) Tests can be conducted in gases other than air.

(3) Gas flow can be metered into the chamber to maintain the oxygen concentration to within prescribed limits. Circulation currents in the chamber are minimized by passing the gas entering the chamber through a porous plate (12 cm in dia) located in the base of the chamber and by exhausting gases through large ducts at the top of the chamber.

(4) The dimensions of the chamber are: ID = 26 cm, height = 53 cm, volume = 28,000 cm^3.

(5) Four windows (three are Pyrex and one is quartz), 12 cm in dia, are provided for viewing and photographing flames.

(6) Rapid depressurization of the chamber can be achieved by actuating the quick opening valve that connects the combustion chamber to a large, evacuated surge tank.

Three types of ignition sources have been used with the combustion chamber: radiative (quartz/tungsten lamp capable of fluxes up to 7 cal/cm^2-sec) conductive (electrically heated wires), and flames (e.g.,

oxygen/CH_4 gas torch). In several of the test series, the onset of flame and self-extinguishment of the flame was detected by changes in the ionization of the gases between two Mo probes.

The fourth experiment in Fig. 5 turned out to be the most effective means of assessing flammability reducing methods. The experiment was used to measure burning rate as a function of pressure and to determine the pressure (p_{DL}) below which ignited propellant will self-extinguish. All of the experimental propellants could be ignited (at least temporarily) by creating a local hot spot. Thus a measure of success of a flammability-reducing method is that it increased p_{DL}. If p_{DL} can be made greater than one atmosphere, then the propellant satisfies one of the major criteria (see Ref. 1). The tests were carried out in the specially fabricated chamber which maintains a prescribed air pressure and introduces fresh air to prevent oxygen depletion during the test. The propellant samples were 0.635 cm cubes mounted on a needle so as to be exposed on all sides. Ignition of the sample was achieved by a carefully controlled pyrogen-type igniter which engulfs the entire sample in flame. In this report, mass burning rates (i.e., the average mass consumption rate of the cube) are reported since they are more repeatable than the linear burning rate data.

B. Free Convection Effects

Several series of color photographs of the ignition and flame development sequences were taken using the arrangement shown in Fig. 7. A motorized (up to 4 frames/sec) 35 mm camera was used to obtain high resolution photographs from which measurements of the flame structure were made. Figures 8 through 12 illustrate the type of flame structure information that is readily obtained from the film sequences. As shown in Fig. 8, burning rate in air is strongly dependent on orientation of the propellant. The burning rate on the bottom of the cylinder is several times greater than the burning rate on the top. Observations such as this support the conclusion that the most severe situation for extinguishment is burning on the leading edge (in the case of Fig. 8, the bottom of the cylinder). Figures 9 and 10 reveal that the flames on the bottom of the horizontal

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cylinder tend to be the most uniform with time. The results of Figs. 9
and 10 tend to support the assumption used in flame models of one-
dimensional (normal to the bottom surface) flames and quasi-steady flame
zone thicknesses. Figures 11 and 12 show the outlines of the flames sur-
rounding the entire cylinder and show the origin of the thickness versus
time plots of Figs. 9 and 10. The differences between the flame structures
of propellant TCC/W-5 (see Table 2 for formulation) without flame retard-
ants is striking.

C. Steady State Burning Rate Measurements

Obtaining steady state burning rate data in air requires a technique
for holding the characteristic length and natural convection influences
constant to produce a steady environment. Figure 13a is a schematic
drawing of an apparatus which was fabricated to obtain burning rate data
in air. The propellant sample is positioned by an adjustable speed drive
device so that the burning surface remains in a constant position with
respect to a surface of prescribed geometry. In this manner, we had
hoped to maintain control over the natural convection effects. The pro-
pellant is temperature conditioned after it is placed in the sample
holder. The material surrounding the sample has sufficient heat capacity
that the sample remained at a nearly constant temperature during the 10
to 20 sec test period. Fig. 13b is a photograph of a prototype version
of the propellant advancing mechanism. The 1.2 cm diameter propellant
sample can be seen protruding from the lower portion of the sample holder.
The photograph in Fig. 14 shows the propellant advancing system mounted
in the previously described atmospheric chamber.

In practice, we were not able to obtain steady state burning data
since the burning was inherently multi-dimensional. For example, in the
downward orientation, atmospheric oxygen increased the burning rate more
on the outer periphery of the cylinder than at the center. Thus, as the
cylindrical test specimen burned, a conical surface evolved which pre-
cluded the determination of a simple one-dimensional burning rate. This
was another indication of the importance of free convection and diffusion
of air. We included this description of an unsuccessful instrument to
alert future investigators of the inherent problems with this type of
measurement.

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IV. EVALUATION OF ADDITIVES

The evaluation of the three types of additives was carried out
using control propellants which represent three major classes of pro-
pellants. As shown in Table 1, the control propellants were: (1) a
well characterized NC/MTN double base propellant which has properties that
are very similar to operational NC/NG propellants, (2) an AP composite
propellant which has been used in a wide variety of previous studies,
and (3) an HMX/PU composite propellant which is known to resist acciden-
tal ignition. It is recognized that AP composite propellants are
unsuitable for gun application because of their very corrosive combus-
tion products. However, one was selected for these studies because
its diffusion flame type of combustion differs greatly from the
premixed flame of conventional nitrocellulose propellants and, thus,
may yield additional insights into the effects of candidate flammability
reducing additives. Other compositions used in the study are
listed in Table 2. Toward the end of this study, an additional series
of propellants were provided by Frankford Arsenal. This series of
propellant will be treated separately in Section V.

The additives which were used in each of the propellant types man-
ufactured at Princeton are summarized in Tables 3, 4, and 5.

A. Halogen Additives to Reduce Propellant Flammability

Various halogen additives were incorporated into nitrocellulose,
AP composite, and HMX composite propellants, and their burning behavior
studied. The formulations of the three control propellants are given
in Table 1. The basis for selecting halogens is given in Section III.A. of
this report.

1. Nitrocellulose Propellants

Ser. (1) Ethylene dibromide -- This compound has been used
successfully as a fire retardant for commercial plastics. It is a liquid
with a boiling point of 132 C. Apparently during the propellant curing
process an appreciable amount of this compound volatilized and the
cured formulation had somewhat less than the intended amount of additive.

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Figure 15, a plot of mass burning rate vs pressure, reveals that adding 3 and 7% of this halogen compound does not produce a useful self-extinguishment point.

Ser. (2) Tetrabromoethylene (C_2Br_4) -- To eliminate the possibility that the additive volatilized during cure, this compound was used. It is a solid and has a melting point of 57 C and a boiling point of 227 C. Thus, during curing of the propellant, the additive should remain incorporated into the mixture. A 10% addition of tetrabromoethylene did not produce any important differences in the mass burning rate vs pressure (see Fig. 16). The corresponding movement of the point of self-extinguishment from less than 0.1 atm to about 0.15 is not encouraging in view of the goal of 1.1 atm.

It was also of interest determine whether there is any affect caused by the structure of the halogen additive. With this in mind the following additives were blended with the control nitrocellulose propellant.

Ser. (3) 1,2,4,5 tetrabromobenzene ($C_6H_2Br_4$) -- This compound is a solid with a ring structure and a melting point of 180 C. A 10% addition of this compound did not produce any significant changes in the mass burning rate vs pressure and point of self-extinguishment, Fig. 17.

Two other ring structure compounds were tried as additives. These compounds contain substitutents (i.e., - OH, - NH_2) which can modify the strength of the halogen bond to the ring through electronic effects. For example, the group may modify the bromine-carbon bond strength making it stronger or weaker depending upon the particular electronic effect of the modifying group. If the bromine-carbon bond is made weaker, then bromine radicals can be formed more easily.

Ser. (4) 2,4,6 tribromophenol ($C_6H_3OBr_3$) -- A solid with a melting point of 120 C. At 10%, this additive did not change significantly the mass burning rate vs pressure of the nitrocellulose propellant, Fig. 18.

Ser. (5) 2,4,6 tribromoanaline ($C_6H_4Br_3N$) -- At the 10% level, this additive caused the propellant to become very soft and unsuitable for testing.

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2. AP Composite Propellants

Ser. (6) Ethylene dibromide -- As in the case of the nitro-
cellulose propellant, appreciable amounts of this additive volatilized
during curing, and the cured formulation did not have the same composi-
tion as the intended formulation. Figure 19, a plot of the mass burning
rate vs pressure, shows no detectable difference in the burning rates of
the control propellant without additive and with 1,3, and 7% of the
halogen compound added.

Ser. (7) 2,4,6 tribromoanaline, and

Ser. (8) 1,2,4,5 tetrabromobenzene were incorporated into the
propellant as additives. The 2,4,6 tribromoanaline at 1% addition
softened the propellant significantly to the extent that it was unsuit-
able for testing. A 10% addition of 1,2,4,5 tetrabromobenzene to the
propellant did not produce either a significant change in the mass burning
rate vs pressure or an improvement in flammability limit (see Fig. 20).

3. HMX Composite Propellants

Ser. (9) Tetrabromo ethylene (C_2Br_4) was incorporated into the
control HMX composite propellant to the extent of 10%. This additive did
not produce a significant reduction in flammability or modification in
burning rate (see Fig. 21).

4. Comments on the Effectiveness of Halogen-Containing Additives

The results of the experiments show that once the propellants
are ignited they will continue to burn and that the halogen additives are
not effective in quenching the flame zone reactions that sustain combus-
tion. If a halogen-containing additive is to be effective in reducing
flammability, it must be broken down to form active radicals which can
then react with the species which would ordinarily sustain the combustion
process. Furthermore, if flame inhibition is to be achieved, the active
radicals must result in a substantial modification of the chemical reac-
tions taking place in the zones near the burning surface and, perhaps,
those on and just below the surface. All of this must take place in an
environment in which the flame retarding intermediate products are rapidly
swept away by the continual flow of gaseous products.

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As an example, consider the mechanism proposed for the burning of nitrocellulose based propellants (see review in Ref. 12);

(1) Subsurface reaction and reaction at the burning surface

$$R - ONO_2 \rightarrow NO_2 + R' - CHO \text{ species}$$
$$\{^{NC}_{NG}\} \qquad \left\{^{H_2CO, \ CH_3CHO,}_{HCOOH, \text{ etc.}}\right\}$$
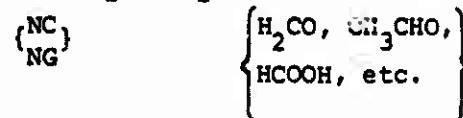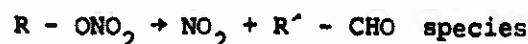
(2) Reactions at the surface and in the fizz zone

$$NO_2 + R' - CHO \rightarrow NO + C-H-O \text{ species}$$
$$\left\{^{H_2CO, CH_3CHO,}_{HCOOH, \text{ etc.}}\right\} \quad \left\{^{CO,CO_2,CH_4,}_{H_2O,H_2, \text{ etc.}}\right\}$$
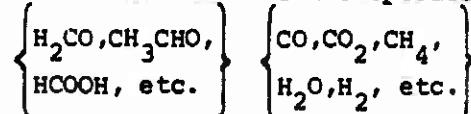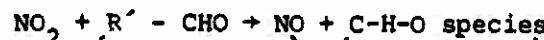
(3) Reactions in the dark zone

$$NO + C-H-O \text{ species} \rightarrow N_2, \ CO_2, \ CO, \ H_2O, \text{ etc.}$$
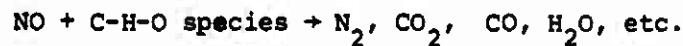
(4) Reactions in the luminous flame zone

$$NO + C-H-O \text{ species} \rightarrow N_2, \ CO_2, \ CO, \ H_2O, \text{ etc.}$$
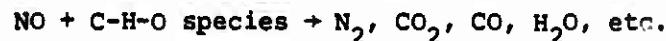
Once the halogen additive decomposes at the burning surface, free radicals are formed which can undergo reaction with species in the propellant flame. In this case the most likely reactive intermediate species are NO_2 and NO. However, the reactions of these critical molecules in the above mechanism are kinetically more favorable than with the halogen radical. As a result, flame inhibition by halogen radicals in nitrocellulose based propellants is not effective.

An important step in normal flame propagation is the chain branching reaction;

$$H\cdot + O_2 \rightarrow OH\cdot + O\cdot$$

The mechanism by which halogen additives are known to inhibit the flammability of hydrocarbons is one involving the interruption of hydrogen free radical chains as formulated above. Accordingly, one explanation for why halogen-containing additives do not reduce the flammability of the nitrocellulose propellant is that the foregoing reaction does not play a major role in controlling the burning rates of nitrocellulose based propellants.

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HMX has flame zone reactions similar to nitrocellulose-based propellants in that the initial step is thought to lead to the production of NO_2,[13]

$$R - NO_2 \xrightarrow{\text{slow}} NO_2 + R\cdot \qquad \text{where} \quad R = C_4H_8N_4(NO_2)_3$$

$$R\cdot \xrightarrow{\text{fast}} CO + CO_2 + NO + N_2 + HCN + N_2O + H_2O + CH_2O$$
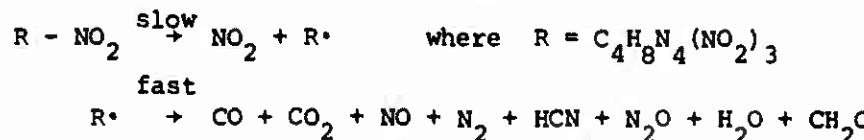
The NO_2 and NO formed by the decomposition reaction can react with the aldehydes and/or the oxygen in the air similar to the case of the nitrocellulose based propellant. Thus, for probably the same reason that halogen additives are ineffective in the introcellulose based propellant, they are also ineffective in the HMX composite propellants.

Since the combustion of AP and AP composite propellants already involve very reactive chlorine-free radical intermediates[14] (e.g., $C\ell\cdot$, $C\ell O\cdot$), the fact that bromine-containing additives do not reduce the flammability of AP composite propellants is not surprising.

B. Phosphorus Additive to Reduce Propellant Flammability

Various phosphorus additives were incorporated into the control nitrocellulose, AP composite, and HMX composite propellants and their burning behavior and flammability reduction evaluated.

1. Nitrocellulose propellants

Ser. (10) Phosphoric Acid (H_3PO_4) -- This compound is a non-volatile liquid with a boiling point of 213 C. It was added to the control propellant to the extent of 5%. This addition produced no significant reduction in flammability or the mass burning rate vs pressure plot (see Fig. 22).

Ser. (11) Ammonium Phosphate ($(NH_4)_2PO_4$) -- This solid compound was added to the control propellant to the extent of 1, 5, and 10%. Even at the 10% level this compound produced no useful reduction in flammability. Incorporating the additive increased significantly the amount of char formed during burning. The mass burning rate vs pressure, Fig. 23, increased at the 5% level but decreased at the 10% level.

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Phosphorus compounds can have several oxidation states, and there seems to be a relation between fire retardancy and the oxidation state. To investigate whether these phosphorus compounds were effective in reducing the flammability of propellants, several formulations were evaluated.

Ser. (12) Triphenyl phosphate $\{(C_6H_5O)_3PO\}$ -- This compound is a solid with a melting point of 50 C and a boiling point of 245 C. It was incorporated into the control propellant to the extent of 10%. It did suppress the mass burning rate significantly at pressures near atmospheric (Fig. 24). Notice that there is only a slight dependence of pressure on mass burning rate and slight reduction in flammability.

Ser. (13) Triphenyl phosphine $\{(C_6H_5)_3P\}$ -- This compound is a solid with the melting point of 79 C and a boiling point greater than 360 C. It was incorporated into the propellant, but during curing the additive caused extensive foaming and reduced it to a soft rubbery state. It was not tested. Phosphine compounds are sensitive to oxidation by oxygen and produce a toxic gas, phosphine. This may be the reason for the foaming.

Ser. (14) Triphenylphosphonium bromide $\{(C_6H_5)_3PBr\}$ -- The use of this compound was suggested as an additive on the basis of synergisms. That is, a synergism may be defined as a case in which the effect of two components taken together is greater than the sum of their effects separately. Many fire retardants are selected on the basis of a synergism. For example, antimony-halogen, phosphorus-halogen synergisms are commonly employed in plastics and polymers to reduce the amount of additive that would be needed to achieve the desired result. The compound when added to the extent of 10% surprisingly increased the mass burning rate (Fig. 25). During testing it was observed that the propellant was easier to ignite and burned more vigorously than the control propellant. There was no flammability reduction.

2. AP Composite Propellants

Ser. (15) Phosphoric Acid (H_3PO_4) -- This non-volatile liquid with a boiling point of 213 C was added to the control propellant to the extent of 1%. With heating the phosphoric acid may undergo reaction with the binder to produce species which can produce cross-linking and char formation. It was observed that the amount of char produced by the incorporation of the acid did not appear to be different than when no acid was added to the composite propellant. The addition of phosphoric acid produced no significant reduction in the mass burning rate vs pressure or in flammability.

Ser. (16) Phosphoric Acid/Urea {5% of a 1 to 4 mixture} -- A mixture of urea and phosphoric acid (or urea phosphate which forms ca. 110 C) has been used to phosphorylate cellulose (at one time on a commercial scale). Processing in the presence of nitrogen compounds has shown that the esterification reaction of the phosphate compound with the hydroxyl group of the cellulose takes place smoothly and rapidly.

$$R - OH + HO - \overset{\overset{O}{\|}}{P} - (OH)_2 + (NH_2)_2CO \rightarrow R - O - \overset{\overset{O}{\|}}{P} - (OH)_2 + 2NH_3 + CO_2$$
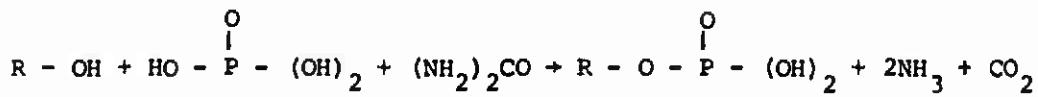
where R is cellulose or some other molecule with an available hydroxyl group. The urea probably functions as a dehydrating agent promoting the phosphorylation of the cellulose.

In terms of the PBAA-Epon system that forms the binder in the AP composite propellant, phosphorylation of the binder probably takes place at a hydroxyl group from the epoxide added as the curing agent in the cure reaction.

Incorporation of the phosphoric acid/urea mixture produces some reduction in the mass burning rate vs pressure, an increased amount of char formation, but no reduction in flammability (Fig. 26).

Ser. (17) Ammonium phosphate {$(NH_4)_2HPO_4$} -- Phosphate compounds may undergo reaction with cellulose or hydroxyl compounds as follows:

$$R - OH + HO - \overset{\overset{O}{\|}}{P} - (ONH_4)_2 \rightarrow RO - \overset{\overset{O}{\|}}{P} - (ONH_4)_2 + H_2O$$

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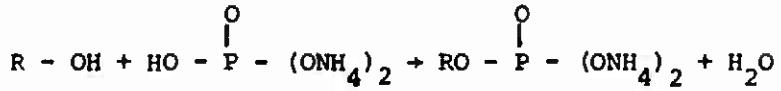
where R is the cellulose molecule or some other molecule with an available hydroxyl group (i.e., the PBAA-Epon System). A series of extensive tests were conducted incorporating ammonium phosphate into the composite propellant. Variables studied included the percent of additive incorporated and particle size. Results are shown in Fig. 27. Even with large amounts of $(NH_4)_2HPO_4$ (10 to 20%), it is ineffective as a char former and is probably acting as a diluent and coolant. Note that the large particle size is more effective, indicating that the burning rate suppressing reaction is probably occurring at the surface.

The small percentages of the additive did not produce significant reductions in the flammability of the propellant. An addition of 5% or more of the additive was significant in reducing the mass burning rate.

Ser. (18) Phoschek-30 -- This compound, ammonium polyphosphate, $(NH_4(PO_3H)_mNH_4)$ was added to the control propellant to the extent of 5%. It produced no reduction in flammability. Unlike the other phosphorus additives (Ser. 15-17), Phoscheck-30 was an effective char former. Large amounts of char were observed forming at the burning surface, and thread-like filaments extended into the flame.

At the same percentage of additive, the Phoschek-30 was more effective in reducing the mass burning rate than $(NH_4)_2HPO_4$ but no flammability reduction was noted.

3. HMX Composite Propellant

Several phosphorus-containing compounds were incorporated into the TCC/W-17 HMX propellant and tested for flammability reduction.

Ser. (19) Phoschek-30 [an ammonium polyphosphate, $NH_4(PO_3H)_mNH_4$] -- This compound was incorporated into the propellant to the extent of 10%. The additive had some effect on reducing the mass burning rate but produced no flammability reduction.

Ser. (20) Ammonium phosphate, $(NH_4)_2PO_4$ was incorporated into the propellant to the extent of 10%. This phosphorus additive had a greater effect in reducing the mass burning rate than the other additives tested. In addition, the flammability of the propellant was reduced significantly. The propellant with $(NH_4)_2PO_4$ additive would not ignite and burn at pressures below 0.45 atm.

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Ser. (21) triphenyl phosphate {$(C_6H_5O)_3PO$}, and

Ser. (22) tritotyl phosphate {$(CH_3-C_6H_4O)_3PO$} -- These compounds were incorporated into the HMX composite propellant to the extent of 10%. Although a change in the structure from triphenyl to tritotyl did exhibit some changs in mase burning behavior, neither additive produced any significant flammability reduction (see Fig. 28).

4. Comments on the Effectiveness of Char Formers

Phosphorus additives in the nitrocelluloss-based propellant do not rssult in any significant reductions in flammability, but burning behavior does change with the kind of phosphorus compound added. The most likely modes of action of the phosphorus additives in the nitrocellulose propellants are as coolants or as free radical inhibitors.

In ths AP composits and HMX compoeits propellants, the PBAA-Epon and polyurethans binders react with the products of the phosphorue compound to promote char formation. However, the effectivenese of the additive depende upon the phorphorus compound and the binder eystem. While char layere seem to work well with inert plaetics, they are ineffective with propellants; the primary factor for this ineffectiveness is the self-oxidizing charactsrietic of the propellant. Once ths propellant is ignited it will continue to burn eince there is a continual feed of oxidizer and fusl fragmente to sustain ths combustion reaction.

In terms of reducing the flammability of the control HMX compoeite propellant, ammonium phosphate [$(NH_4)_2PO_4$] is the moet effective. As shown in Fig. 28, at the 10% levsl $(NH_4)_2PO_4$ increased p_{DL} from 0.1 to 0.45 atm, an encouraging indication.

C. Coolants as Additives to Reduce the Propellant Flammability

Sevsral compounds, both organic and inorganic were incorporated into the thrse types of propsllants and evaluatsd ae coolants in reducing flammability.

1. Nitrocellulose Propellants

Ser. (23) Urea {$(NH_2)_2CO$} -- This organic compound has a melting point of 133 C and decomposee with further heating. It wae incorporated into the propellant to the extent of 10%. Examination of the mass burning

rate vs pressure plot (Fig. 29) reveals that urea does act as a coolant in the near atmospheric pressure region but seems to be ineffective in the low pressure regions.

Ser. (24) Oxamide $\{(NH_2)_2(CO)_2\}$ -- This organic compound has a melting point of 180 C and decomposes at a much higher temperature. It was incorporated into the propellant to the extent of 10%. Examination of the mass burning rate vs pressure plot (Fig. 29) shows that there is a very significant reduction of the mass burning rate over the entire pressure region examined. Note the similarity with the formulation using urea -- a high suppression in the region near atmospheric pressure and a lower suppression in the sub-atmospheric pressure region. However, oxamide with a similar chemical structure and a higher melting point coupled with a higher heat of decomposition is more effective than urea. Neither compounds, however, show any effectiveness so far as reducing the flammability.

2. AP Composite Propellant

Ser. (25) Potassium ferricyanide and

Ser. (26) Ammonium bromide $\{NH_4Br\}$ -- These compounds were incorporated into the control AP composite propellant and evaluated as flammability reducing agents. The incorporation of 5% potassium ferricyanide as an additive to the control propellant did not reduce flammability, see Fig. 30. It was noted that glowing particles (e.g.,iron oxides) form in the flame and serve to indicate the particle track and extent of decomposition. Even though particle size was not controlled, it was noted that the large particles passed through the flame with little reaction, whereas smaller particles decomposed in the flame near the surface.

The effect of the large decrease in burning rate with the ammonium bromide additive may be attributed to its rather high sublimation temperature of 542 C. This is close to the temperature of the burning propellant surface. The large amount of energy required to sublime and/or decompose the ammonium bromide at or near the propellant surface is thus reflected in a marked decrease in the burning rate, see Fig. 30.

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Ser. (27) Urea {$(NH_2)_2CO$} -- This compound, with a melting point of 133 C, was incorporated into the propellant to the extent of 5%. Examination of the mass burning rate vs pressure plot, Fig. 30, shows that there is no reduction in flammability and little change in burning rate. The relatively large exothermic effects of the burning propellant far overshadow the endothermic decomposition of the urea.

3. HMX Composite Propellant

Two compounds were incorporated into the HMX composite propellant and evaluated as coolants.

Ser. (28) Ammonium Carbonate {$(NH_4)_2CO_3$} -- This solid with a decomposition temperature of 58 C was incorporated into the propellant to the extent of 10% and did not produce any reduction in flammability (Fig. 31).

Ser. (29) Ammonium Sulfate {$(NH_4)_2SO_4$}--This eolid with a decomposition temperature of 235 C wae incorporated into the propellant to the extent of 10% and produced a emall reduction in the mass burning rate but no flammability reduction, eee Fig. 31.

4. Comments on the Effectiveness of Coolants

Several compounds were incorporated into the three control propellants (e.g., nitrocelluloee, AP composite, and HMX compoeite) to evaluate their potential as coolante. The most effective coolants are those with decomposition temperaturee near that of the surface temperature of the burning propellant. Compounds with low melting or decomposition temperaturee ehow little effect. Although the coolants produce changes in the maes burning rate with preesure, they do not significantly increaee P_{DL}.

When oxamide is added to the nitrocellulose-based propellants (which have relatively low surface temperatures), the following are observed:

(1) Oxamide increases P_{DL} in N_2 (Fig. 32) but not in air.

(2) Oxamide has a pronounced effect on the gas phase temperature profile (Fig. 33) but no clearly discernible effect on the propellant surface temperature.

(3) Oxamide does not make the propellant more difficult to ignite (see Fig. 8a in Ref. 1) using a quartz/tungsten lamp. (The decrease in ignition time is probably a result of the oxamide decreasing the transmissivity of the propellant.)

The proposed explanation of all three observations is the same: since the surface temperature of the matrix propellant is lower than the decomposition temperature of oxamide, the endothermic decomposition of the oxamide is not centered at the propellant surface. However, there is a slight contribution from the oxamide (in the flame zone), i.e., since at the 5% level, oxamide produces a 20% reduction in burning rate (see Fig. 32).

To further explore the effect of additives whose decomposition temperatures are higher than the surface temperature of the matrix propellant, ammonium perchlorate (AP) was added to the control nitrocellulose-based propellant. AP is known to have a higher surface temperature than NC double base propellants. AP (even though it is an oxidizer) did not affect appreciably the ignition limit of the NC double base propellant.

Finally, the ignition data (see Fig. 8c in Ref. 1) for the HMX/PU propellants support the premise that the surface temperature of the matrix propellant must be relatively high for the coolant to function as a flammability suppressant. As shown in Fig. 8c in Ref. 1, oxamide has a profound influence on the ignition characteristics. The data of Table 6 show that the surface temperature of the HMX composite propellants is much higher than the surface temperature of either an AP composite or NC double base propellant. Indeed, for radiant heat fluxes less than 5 cal/sec-cm^2 the propellant containing 10% oxamide (TCC/W-4) is not ignited by the radiation from the quartz/tungsten lamp. However, it must be noted that when the propellant is gasified and not ignited, the gases that emanate from the propellant surface are easily ignited by an open flame.

D. Organometallic Compounds

Organometallic compounds of different types are known to react with the intermediate products.[9,10] Perhaps a specific compound can be

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incorporated to react with one of the major oxidizing gases and reduce the energy liberated during the combustion reaction or, at least, to tie up the active species and achieve some degree of flame inhibition. With these ideas in mind some preliminary experiments were carried out using simple organometallic compounds of similar structure to determine what effect they would have on reducing flammability:

(1) triphenylmethane $(C_6H_5)_3CH$ was used primarily as a control additive to see what effect this particular structure had on the propellant.

(2) tetraphenyl lead $(C_6H_5)_4Pb$ and tetraphenyl tin $(C_6H_5)_4Sn$ added to the control nitrocellulose-based propellant to the extent of 10% exhibited the following effects (Fig. 34). The tetra-phenyl tin had the effect of reducing the mass burning rate, while the tetraphenyl lead compound accelerated the burning rate (somewhat) at pressures near atmospheric (it is known that some lead compounds act as catalysts for the reaction of $NO_2 \rightarrow NO$ and $NO \rightarrow N_2$). Whether this is happening here is not known. The corresponding organotin compound had a significant effect on reducing the burning rate as compared to the lead compound. Obviously the metal plays an important part in modifying the burning behavior. Larger amounts of char and a flame containing more carbon were significant observations obtained with the organotin additive. Neither additives significantly reduced flammability.

E. Enthalpy and Gas Composition Measurements of Coolants and Binders*

Two experimental techniques were used to measure the enthalpy changes that are associated with several candidate coolants. Differential Thermal Analysis (DTA) was used on coolants and a combination of DTA and Thermal Gravimetric Analysis (TGA) was applied to both coolants and binders. A more direct measurement of the energy change exhibited by

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*This section is based on experimental data provided by R. A. Biddle of the Elkton Division of the Thiokol Corp.

the coolants was made by using Differential Scanning Calorimetry (DSC). These analyses were run on samples of approximately 10 mg under a nitrogen atmosphere at a scanning speed of 10 C/minute.

The binders tested exhibit both an initial small exotherm and a significantly larger endotherm. Hydrocarbon binders, such as the carboxyl-terminated polybutadiene (CTPB) and the hydroxyl-terminated polybutadiene (HTPB), undergo the initial exotherm at 375-380 C with the carboxyl-terminated binders exhibiting the largest enthalpy change. This is also the case for the subsequent endotherm in both of these binders. Here this endothermic process occurs at 480-486 C. The relative magnitudes of these changes are shown in Table 7. The polyester binder shows reduced magnitudes for both the initial exotherm (-18 cal/g) and the subsequent endotherm (+124 cal/g) occurring over a narrow temperature range that is intermediate to the hydrocarbon-type binder changes (~ 430 C).

Examination of the coolants was made by both DTA/TGA and DSC techniques. Results for three coolants are shown in Table 7. The endothermic changes that occur on heating these coolants have increasing magnitudes on going from melamine to oxamide. Various values of the endothermic change have been measured for the melamine by the DSC technique, depending upon the rate of heating and the sample size. However, there is general agreement in the order of magnitude of the endotherm measurements between the two techniques. Melamine starts to evolve ammonia at about 546 C and this continues up to the melting point of 633 C. Analysis of the oxamide by the DTA/TGA techniques showed sublimation only, whereas, in the DSC technique, there is probably an attendant endothermic decomposition which accounts for the additional heat absorbed.

These data serve to show that both the binders and the coolants undergo thermal changes in the same general temperature range and that there are different types of decomposition reactions occurring for the various coolants. There is also a gradation of the magnitude of the endothermic processes involved with the coolants.

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The gases evolved by the individual coolants were analyzed by a flash pyrolysis technique using a 1200 C pyrolsis probe with a 1 to 2 mg sample. The gases generated were passed through two gas chromatographic columns in series, selected to separate N_2, CO, H_2O and NH_3 for subsequent measurement. Helium carrier gas was used to transport these gases through the separation columns and the detector assembly. Typical results for the identified product gases from the three coolants of interest are shown in Table 7. Here it can be seen that melamine produces mainly nitrogen and ammonia, whereas oxamide produces predominantly carbon monoxide. There is a complicating feature in each of these analyses in that there is an unknown component which was not identified. For the melamine, approximately one-third of the total gases was not identified and are not included in the values shown in Table 7. The unidentified gases could be largely hydrogen cyanide and cyanogen. Only seven percent of the gases were not identified from the oxamide.

F. Hazards Associated with Smoldering Propellants

Several of the propellants could be heated to the point of smoldering (i.e., sub-surface reactions under a char layer) without developing either the self flame or the diffusion flame. The gaseous products from the smoldering represent a serious hazard since they are extremely flammable. For example, a smoke column 20 cm above TCC/W-4 smoldering under room conditions can be easily ignited with a match; the flame flashes down the column and produces a flame on the sample. If these gases are allowed to collect in a closed space a serious fire and explosion hazard exists. Juhasz and Rocchio[15] analyzed these gases and found they contained large fractions of CO, NO, and H_2O.

Elimination of smoldering is a difficult task because the smoldering reactions of several of the propellants are independent of the ambient air. For example, a 75% HMX, 15% PU, and 10% oxamide propellant will continue to smolder in one atmosphere of N_2 or in its own combustion products. At the 20% oxamide level, sustaining the smoldering requires air.

The smoldering also produced complications with several of the experiments in which we intended to extinguish burning propellant specimens. For example, it was relatively easy to extinguish a 75% HMX, 15% PU, and 10% oxamide propellant immediately after ignition (before a char layer develops). However, after the propellants had burned and formed a char layer several millimeters thick, the smoldering at the char/unburned propellant interface persisted after the visible flame was extinguished by direct impingement of CO_2 flow. In many instances, the smolder would continue for several seconds, and, then, the visible flame would re-establish itself.

V. IGNITION AFTER EXPOSURE TO FLAMES

A. Results of Flame Tests

During the course of the Army's program to develop high energy, low
flammability propellants, several organizations supplied Frankford Arsenal
with candidate propellants. It was of interest to obtain a relative com-
parison of the ignition properties of these propellants. Shock Hydro-
dynamics, Inc. tested these propellants for impact sensitivity[16]*and
Calspan[17] tested several of the propellants for cook-off during slow
heating. Frankford Arsenal molded the eight formulations shown in Table
8 into cylinders 0.95 cm in diameter and 2.5 cm long. The cylinders were
tested using the apparatus shown in Fig. 6 (specimen mounted vertically).

The test sequence consisted of mounting the cylinder vertically on
a flat plate so that free convection effects would be reduced and subject-
ing it to a calibrated acetylene flame until first flame was observed. The
time of first flame was determined by examining color movies of the tests.
Following the observation of first flame on the propellant, the acetylene
flame was quickly moved away from the sample to determine if the propellant
would self-extinguish. If the propellant specimen did not self-extinguish,
the specimen was extinguished by a low velocity jet of CO_2. The tests
were repeated five times.

The results of the tests are shown in Fig. 35. It should be noted
that the tests were not meant to achieve a relative ranking of the propel-
lants. Such a rank would be meaningless since the energy levels of the
propellant vary greatly and some of the propellants are intended for use
as relatively low energy outer layer materials and others are intended
to be high energy propellants. Test-to-test variations of 1 to 2 seconds
are not uncommon.

To obtain insights into how the hazards associated with low flammabil-
ity propellants compared to the hazards of more conventional materials, a
widely used ball powder (WC 846) protected by a thin (0.025 cm) brass sheet,
the control nitrocellulose-based propellant, and M-9 propellant were
subjected to the same ignition conditions as the low flammability specimens.

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*Shock Hydrodynamics, Inc. also carried out radiative ignition, ignition
by hot spall, and sample-to-sample flame spreading tests.

Several of the propellants are significantly more resistant to ignition than either the control nitrocelluloss propellant or M-9. However, the WC 846 ball powder protected by brass was generally mors rssistant to ignition.*

The compositions with impetus values less than 250,000 ft-lbf/lbm are intsnded to be used as outer laysrs on a main propellant charge. Since these outer layers make up a small percentage of the total charge weight, greatsr improvemsnts in system flammability can be achieved by sacrificing some of the energy in outer layers. Note that only one of thsse outer layer materials self-extinguishes when the acetylene flame is removed.

The results of Tabls 8 should be a source of encouragement since they indicate that ignition energy requirements of the low flammability propellants are greater than for several conventional double base propellants and, in several cases, comparable to brass protected ball powder.

B. Effect of Low Heatiiig Rate on Conditions for Ignition and Self-Extinguishment

The time of self-extinguishment following ignition is strongly dependent on the temperature profile in the condensed phase when ignition occurs. The basis for this is that a propellant conditioned at a relatively high temperature (e.g., 60 C) will be more likely to have sustained combustion than a propellant conditioned to ɩ relatively low temperature (e.g., -20 C). Similarly, a propellant that is ignited by a very low heat flux will be preheated to a significant depth prior to ignition. Thus after a preheated propellant is ignited, it burns with a more vigorous flame than a comparable propellant which was ignited very rapidly. The self-extinguishment of the propellant becomes more likely as the layer preheated during ignition is burned off. Propellants that smolder and, thus, burn very slowly, develop increasingly thick thermal waves which, in effect, preheat ths propellant.

Figure 36 illustrates the manner by which slow heating alters self-

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*In a similar test reported in Ref. 1, a lower energy ꓶMX composite propellant (75% HMX, 15% PU, and 10% oxamide) proved to ᵇᵉ more resistant than the brass protected WC 846.

extinguishment. Figure 36 shows the steady state relationships between burning rate (r), ambient pressure (p), surface temperature (T_s) and depth of thermal profile (δ_b). Increasing heat flux to the surface during steady burning (q_b) decreases the thickness of the preheated layer (δ_b); decreasing the ignition heat flux (q_i) increases the depth of the preheated layer when ignition occurs (δ_i). Figure 36 is for the situation in which the depth of the preheated region at ignition is much larger than the preheated depth during steady state burning.

As shown on Figure 36, when the heat-up-to-ignition is slow, there is a period of time [approximately equal to the time required to burn off the thickness $(\delta_i - \delta_b)$] during which the low flammability characteristics of the propellant are not fully realized.

The above discussion introduces a rather complex question concerning how to reduce flammability over the entire range of heating conditions. Of course there is an initial temperature above which all propellants will burn vigorously.

VI. CONCLUSIONS

The goal of the invsstigation summarized in this rsport was to obtain
an understanding of how additives intended to reduce flammability affect the
low pressure combustion characteristics of high energy propellants. The
approach to reducing flammability csntered on the use of additives which
when used with plastics are known to suppress gas phase reactions, to
promots char formation, or to promote endothermic surface reactions. Combustion
limits or flame retention limits sxist for all solid propellants, although
these limits may be at sub-atmospheric pressurss. The aim of adding rate
retardants, char-formers, and coolants is to move ths extinguishment
boundaries above 1 atm pressure at 140 F ambient temperature.

Based on the rssults of this invsstigation, it is now apparent that
the continual resupply of reactants which sustain the combustion reactions
far overwhelms any action of ths additive (in small quantities) to reduce
flammability. One fact is clear, once high energy propellants are ignited
in air, thsy tend to continue to burn (or smolder) primarily through the
continual rssupply of reactants (boch from the propellant itself and the
ambient air). The propellant modifications reduced burning rates but did not
significantly increase the pressure at which self-extinguishment occurred.

The development of a self-extinguishing (under ambient conditions),
high energy propellant is a goal yet to bs achieved. However, lower
energy materials suitable for use as an outer-layer protective coating
(which is consumed as an energetic material under the desired high pressure
operating conditions) appear to be promising. Two of the conventional
methods of reducing flammability, flame inhibitors and char formers, have
been explored well beyond the range of practical limits and found to be
ineffective whsn used with propellarts. The use of coolants with the
high decomposition tempsrature composite propellants (e.g., HMX/polyurethane)
is effect.ve in reducing flammability at the expense of propsllant energy.

In the course of these studies, the explosion and fire hazards of
gassous products which evolve from smoldering propellants were recognized.
Conventional propellants burn with vigorous flamss that generate products
that are not liksly to produce explosion hazards. The observed smoldering,
which only partially decomposes the propellant, is a direct rssult of
efforts to rsduce flammability.

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In 1970, Grsen, Visnov and Krafcik[18] published a survsy of the status of fundamsntal ignition concepts and how they related to reducing the vulnerability of propellants. In retrospect, their recommendations (e.g., to conaider propellants other than nitrate satsrs, to use protective outer-layer coatings, and to develop tests that simulate hazards under field conditions) were sound.

The studies to date have shown that sslf-extinguishment limits and ignition resistance must be defined with respect to some limits on thermal abuse. For example, any high energy material will burn if heated to a sufficiently high temperature over a prescribed time. Thus, additional attention must be directed at the task of developing tests for ranking the relative hazards of propellants under conditions that can be related to operational hazards. The tests must take into account the applications for which the propellants are intended and the protective packaging that will be used in the field. In many respscts, the various flammability and ignition tests unnecessarily penalize some of the propellants. For exampls, the propellants will not be used as a single exposed cylinder of propellant; they will be protected by a container. Thus, in the future, tests of vulnerability to the various ignition hazards should include evaluations of complete systems.

To date, a large part of the flammability investigations conducted throughout the country have been directed at finding additives that would, when used in small percentages, make either nitrate ester propellants or nitramine composite propellants self-extinguish at atmospheric pressure. The break-through of finding such additives or the development of new ingredients is the prefsrred solution. however, it is now apparent that the usual fire retardants are not effective when used with self-oxidizing, high energy propellants. Attention should now be directed at understanding how the low pressure propellant decomposition processes that produce reactive intermediates and the subsequent reactions with air can be inhibited. Thus, a more detailed knowledge of the chemistry is required.

The fact that self-extinguishment of high energy propellants is observed at 0.3 atmospheres of air reveals that the sought-after physical effect exists. Thus, the research task is to move the self-extinguishment boundary from 0.3 to 1.1 atmospheres of air.

APERÇU

The Army's program developed high energy propellants with reasonable physical properties and greatly reduced flammabilities. However, the bare propellant exposure conditions proved to be unrealistically severe and not representative of the operational environment. The application payoff of this research will be achieved in future development programs that utilize the low flammability propellants in lightweight magazines which offer minimum protection to the propellants.

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GLOSSARY

Ammonium oxalate	coolant [$(NH_4)_2C_2O_2 \cdot H_2O$]
AP	ammonium perchlorate
CTPB	carboxyl terminated polybutadiene binder system
CuSa	monobasic cupric salicylate
DOP	dioctyl phthalate
DSC	differential scanning calorimeter
EC	ethyl centralite (a stabilizer)
EPON 828	epoxy (diglycidyl ether of bisphenol A)
ERL 0500	epoxy (N,N-diglycidyl-p-aminophenyl ether)
HIT	high ignition temperature
HMX	$(CH_2NNO_2)_4$; beta-HMX
HTPB	hydroxyl terminated polybutadiene binder system
MTN or TMETN	trimethylol ethane trinitrate (metriol trinitrate)
NC	nitrocellulose (typically 12.6% N)
NG	nitroglycerine
Oxamide	coolant ($NH_2COCONH_2$)
PBAA	polybutadiene acrylic acid binder system
PbSa	lead salicylate
P_{DL}	pressure below which a propellant will not burn
Phoschek-30	ammonium polyphosphate $NH_4[PO_3H]_mNH_4$
PNC	particulate nitrocellulose (typically 12.6% N)
PU	polyurethane binder system
SEAP	self-extinguishing at atmospheric pressure
TAGN	triaminoguanidine nitrate
TCC/W	Wasatch Division of the Thiokol Chemical Corp.
TEGDN	triethylene glycol dinitrate
TGA	thermal gravimetric analysis

Table 1

CONTROL PROPELLANTS

Control Nitrocellulose Based Propellant[a]

Nitrocellulose (PNC), 12.6% N_2	53.70%
TMETN	39.10
TEGDN	7.02
EC[b]	0.08
Carbon Powder	0.10

Control AP Composite Propellant

Ammonium Perchlorate (30% 5μ + 70% 45μ)	75%
PBAA (85.6%) + EPON828 (14.4%)	25%

Control HMX Composite Propellant[c]

Binder (Isonate 136T, Carbowax-400, TMP, and FeAA)	25%
HMX	75%

where
Isonate 136T is 3,3'-Bitolylene 4,4'-Diisocyanate.
Carbowax-400 is hydroxyl-terminated polyethylene oxide of 400 molecular weight.
TMP is trimethylolpropane trimethacrylate.
FeAA is ferric acetylacelonate.

[a]The propellant is a castable plastisol which uses particulate nitrocellulose (PNC) with a mean diameter of 5μ as its main ingredient

[b]Because each of the ingredients,PNC, TMETN, and TEGDN contain the stabilizer ethyl centralite (EC), the total EC in the propellant is 1.7%.

[c]The ingredients were received from the Wasatch Division of the Thiokol Corp. in a partially processed form. Experimental propellants were made by blending in the additives and then curing the resulting mixture at 95 C for 2 hours.

Table 2

SUMMARY OF PROPELLANT FORMULATION
OTHER THAN CONTROL PROPELLANTS

DESIGNATION	FORMULATION
TCC/W-4[a]	75.0% HMX, 15.0% polyurethane binder containing 0.4% P in the form of Phoschek-30, 10.0% oxamide
TCC/W-5[a]	83.33% HMX, 16.66% polyurethane
WC 846	81% NC (13.15% N), 10.0% NG, 5.8% debutylphalate, 1.0% diphenylamine, 0.4% graphite, 1.0 to 1.5% other volatiles
M-9	57.75% NC (13.15% N), 40% NG, 1.5% KNO_3, 0.75% diphenylamine (composition may be diluted by residual volatiles)

[a] Supplied by the Wasatch Division of the Thiokol Corp.

Table 3

SUMMARY OF ADDITIVES INVESTIGATED TO REDUCE

FLAMMABILITY OF NITROCELLULOSE PROPELLANTS

TABLE 4

SUMMARY OF ADDITIVES INVESTIGATED TO REDUCE FLAMMABILITY OF AP COMPOSITE PROPELLANTS

ADDITIVE	ADDED %	BATCH NUMBER	WHY ADDED AND THEORY	PRES. OF SELF-EXTING. (ATM)	SURFACE/RESIDUE	GENERAL COMMENTS
NONE	0	1103	CONTROL	0.08	VERY SMALL AMOUNT OF CHAR LEFT AS RESIDUE.	NONE
ETHYLENE DIBROMIDE	1,3,7	1103 A,B,C	PREVIOUSLY USED AS FIRE RETARDANT FOR COMMERCIAL PLASTICS. HALOGEN COMPOUND MAY DECOMPOSE TO YIELD SPECIES WHICH SCAVENGE ACTIVE SPECIES OF COMBUSTION REACTIONS, OR FORM NONCOMBUSTIBLE GAS TO SUPPRESS FLAME.	0.15	CHAR LEFT AS RESIDUE. BUT NOT MORE THAN CONTROL.	NO CHANGE IN BURNING RATE.
1,2,4,5 TETRABROMOBENZENE	10	1103N	MAINLY HALOGENATED RING COMPOUND. DETERMINE EFFECT OF HALOGEN ADDED BY RING STRUCTURE. MODE OF ACTION SIMILAR TO ABOVE.	0.15	CHAR LEFT AS RESIDUE. NOT MORE THAN CONTROL.	NO CHANGE IN BURNING RATE.
2,4,6 TRIBROMOANALINE	1	1103J	DIFFERENT SUBSTITUENTS ON RING MAY EFFECT RELEASE OF HALOGEN. MODE OF ACTION SIMILAR TO ABOVE.	NOT TESTED	---	---
PHOSPHORIC ACID	1	1103L	NONVOLATILE ACID. MAY FORM LIQUID LAYER ON BURNING SURFACE, OR PHOSPHORYLATE ACTIVE GROUPS TO ALTER DECOMPOSITION MECHANISM.	0.10	NO SIGNIFICANT CHAR LEFT AS RESIDUE.	NO CHANGE IN BURNING RATE.
PHOSPHORIC ACID/UREA MIXTURE	5	1103M	MIXTURE HAS BEEN USED TO PHOSPHORYLATE CELLULOSE. MAY ALSO WORK ON PBAA-EPON BINDER SYSTEM WITH AVAILABLE HYDROXYL GROUPS. MAY ALSO ALTER OR CHANGE DECOMPOSITION MECHANISM.	0.10	SOME RESIDUE LEFT AFTER BURNING. NOT MORE THAN CONTROL.	VERY LITTLE CHANGE IN THE BURNING RATE.
AMMONIUM PHOSPHATE $(NH_4)_2HPO_4$	1,5,10, 15	1103G	ACTION PRIMARILY AS A COOLANT. PHOSPHORUS COMPOUND MAY ALSO ACT AS CHAR FORMER BY YIELDING ACIDIC FRAGMENTS UPON DECOMPOSITION.	0.1 to 0.6	APPRECIABLE AMOUNT OF CHAR LEFT AS RESIDUE.	POL. AND DECREASE IN BURNING RATE DEPENDENT UPON AMOUNT OF ADDITIVE IN PROPELLANT.
PHOSCHEK-30 $NH_4(PO_3H)_m NH_4$	5	1103E	PRIMARILY A CHAR PROMOTER. ALTERS DECOMPOSITION OF PROPELLANT BINDER BY FORMING ACIDIC FRAGMENTS WHICH REACT WITH BINDER.	0.18	APPRECIABLE AMOUNT OF CHAR LEFT AS RESIDUE.	SIGNIFICANT DECREASE IN BURNING RATE.
POTASSIUM FERRICYANIDE	5	1103P	MODE OF ACTION AS COOLANT. TAKES UP HEAT IN DECOMPOSITION THAT WOULD OTHERWISE BE SUPPLIED TO PROPELLANT. MAY FORM SOLID PARTICLES IN FLAME THAT MAY SUPPRESS FLAME REACTIONS.	0.15	NO SIGNIFICANT CHAR LEFT AS RESIDUE.	NO SIGNIFICANT CHANGE IN BURNING RATE.
AMMONIUM BROMIDE NH_4Br	5	1103I	HIGH HEAT OF SUBLIMATION TEMPERATURE MAY BE MORE EFFECTIVE THAN COMPOUNDS WHICH DECOMPOSE AT LOWER TEMPERATURES. MODE OF ACTION SAME AS ABOVE.	0.20	CHAR LEFT AS RESIDUE. MORE THAN CONTROL.	LARGE DECREASE IN BURNING RATE DUE TO HIGH SUBLIMATION TEMPERATURE.

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SUMMARY OF ADDITIVES INVESTIGATED TO REDUCE FLAMMABILITY OF HMX COMPOSITE PROPELLANTS

ADDITIVE	ADDN %	BATCH NUMBER	WHY ADDED AND THEORY	PRES. OF SELF-EXTING. (ATM)	SURFACE/RESIDUE	GENERAL COMMENTS
NONE	--	HMX-17	CONTROL	0.10	BURNED VERY UNIFORMLY WITH ONLY SMALL AMOUNT OF CHAR ON SURFACE	NONE
TETRABROMO-ETHYLENE	10	HMX/PJ-17A	SOLID NONVOLATILE HALOGEN COMPOUND THAT DID NOT EVAPORATE DURING CURE. HALOGEN COMPOUND MAY DECOMPOSE TO YIELD SPECIES WHICH COULD SCAVENGE COMBUSTION REACTIONS OR FORM NON-COMBUSTIBLE GAS TO SUPPRESS FLAME.	0.15	CHAR LEFT AS RESIDUE; BUT NOT MORE THAN CONTROL	NO SIGNIFICANT CHANGE IN BURNING RATE AS COMPARED TO CONTROL
AMMONIUM PHOSPHATE $(NH_4)_2PO_4$	10	HMX/PU-17B	DECOMPOSING PHOSPHORUS COMPOUND FORMS ACIDIC FRAGMENTS THAT CAN ACT UPON BINDER TO MODIFY OR ALTER DECOMPOSITION TO PRODUCE CHAR.	0.40	CHAR LEFT AS RESIDUE MORE THAN CONTROL	ADDITIVE CAUSES MARKED CHANGE IN BURNING BEHAVIOR AND SIGNIFICANT INCREASE IN P_{DL}
PHOSCHEK-30	10	HMX/PU-17C	MODE OF ACTION SAME AS ABOVE.	0.20	APPRECIABLE AMOUNT OF CHAR LEFT AS RESIDUE.	SAME AS ABOVE
TRIPHENYL-PHOSPHATE $(C_6H_5O)_3PO$	10	HMX/PU-17D	ORGANIC PHOSPHORUS-OXYGEN COMPOUNDS MAY BE MORE EFFECTIVE IN PROMOTING CHAR LAYERS THAN OTHER PHOSPHORUS ADDITIVES.	0.15	CHAR LEFT AS RESIDUE; BUT NOT MORE THAN CONTROL.	BURNING RATE SIGNIFICANTLY REDUCED, BUT NO FLAMMABILITY REDUCTION.
TRITOTYL-PHOSPHATE $(CH_3-C_6H_4O)_3P$	10	HMX/PU-17E	SAME MODE OF ACTION AS ABOVE. STRUCTURE OF ADDITIVE DIFFERS SLIGHTLY FROM THE ONE ABOVE, MAY SHOW INCREASED CHAR LAYER FORMATION.	0.15	SAME AS ABOVE	SAME AS ABOVE
AMMONIUM CARBONATE $(NH_4)_2CO_3$	10	HMX/PU-17F	MODE OF ACTION AS COOLANT. DISSIP.. ENERGY AND DECOMPOSES OR MELTS SURFACE. FORMS NONCOMBUSTIBLE GAS.	0.1	SAME AS ABOVE	NO CHANGE IN THE BURNING RATE AS COMPARED WITH CONTROL.
AMMONIUM OXALATE	10	HMX/PU-17G	SAME APPLIES HERE AS ABOVE. COMPOUND HAS A MUCH HIGHER MELTING TEMPERATURE THAN THE CARBONATE.	0.15	SAME AS ABOVE	SLIGHT CHANGE IN BURNING RATE WITH THIS COOLANT.

Table 6

Combustion and decomposition temperatures of propellants and propellant ingredients.

Temperature	PROPELLANT TYPE			COOLANT
	NC/MTN	AP COMPOSITE	HMX COMPOSITE	Oxa-mide
Theoretical isobaric flame temperature of principle oxidizer burning as a monopropellant. K	$\sim$2500	1405	3275	--
Temperature of decomposition at slow heating rate, K	$\sim$460[a] (Hot Plate)	$\sim$670[b] (DSC)	$\sim$535[b] (DSC)	$\sim$506[c]
Theoretical isobaric flame temperature of propellant, K	2537 (With 39% MTN and 7% TEGDN)	2850 (With 15% PBAA)	1940 (With 15% PU)	--
Condensed phase surface temperature during low pressure burning, T_s, K	$\sim$500[a]	700-900[d]	$\sim$1050[c]	--

[a]Kubota (Ref. 12)
[b]Derr, et al (Ref. 19)
[c]Biddle (Ref.20)
[d]Steinz, et al (Ref. 21)

Table 7

Chemical analysis of binders and coolants

Flash pyrolysis of coolants:
Identified Gas Product, percent by weight

Coolant	CO_2	CO	N_2	NH_3	H_2O
Melamine	-	6	46	48	-
Oxamide	1	69	13	15	2

Thermal decomposition of coolants:

	Combined DTA and TGA			DTA	
	T at peak, C	h cal/g	T at start, C	Gas evol.	h cal/g
Melamine	384	+272	273	Starts (NH$_3$?) up to melting at 360 C	+102 to +295
Oxamide	332	+452	233	Sublimation only	+350
Ammonium sulfate	338	+251	234	Starts	-
	443	+1028	330	Rapid with melting	-

Thermal decomposition of binders:

Binder	Temp at Peak, C	Enthalpy, cal/g
CTPB/ERL-0500	375	-239
	480	+786
HTPB (R45-DDI)	381	-143
	486	+409
Polyester (F-1747-ERL)	434	-18
	454	+124

TABLE 3

SAMPLES PROVIDED BY FRANKFORD ARSENAL FOR FLAME IGNITION TESTS*

DESIGNATION	SOURCE	ACTIVE INGREDIENTS	BINDER	FLAMMABILITY REDUCING ADDITIVE	IMPETUS FT-LB/LB	AVERAGE OF 5 TIMES TO FIRST FLAME, SEC	RELATIVE IGNITION TIMES
1. TGP-7312-030	THIOKOL/WASATCH	HMX 85%	POLYURETHANE	--	>400,000	3.2	2
2. CASOL	ROCKETDYNE	TAGN 55%	ETHYL CELLULOSE TRIPHENYL PHOSPHATE	OXAMIDE	<200,000	5.4	1
3. PPL 6180	PICATINNY ARS.	HMX 70% (d_m ~2μ)	TUFFLEX 25.5% DOP 4.5%	0	227,000	3.6	2
4. PPL 6217	PICATINNY ARS.	TAG PICRATE 69% HMX 10%	SAME AS PPL 6180	?	~150,000	2.4	3
5. PPL 6151	PICATINNY ARS.	HMX 16% TAGN 54%	SAME AS PPL 6180	0	~170,000	2.5	3
6. PPL 6152	PICATINNY ARS.	HMX 25% TAGN 45%	SAME AS PPL 6180	0	~140,000	2.7	3
7. HES 8602.2	HERCULES/ FRANKFORD ARS.	HMX 74.0% NC (12.6%N)7.5% BDNPA 10.0%	CELLULOSE ACETATE 4.2% SANTICIZER M-17 3.6%	0	>400,000	3.6	2
8. HES 8028	HERCULES/ FRANKFORD ARS.	HMX 84%	SALICYLIC ACID,0.16% HYCAR 2121-X-66 (POLYACRYLIC 15.84%)	0	>364,000	5.3	1
M-9	U.S. ARMY	NC 57.8% NG 40.0%			382,000	1.2	-
CONTROL NC BASED PROPELLANT	PRINCETON	TABLE 1				2.2	-
WC 846 BALL POWDER PROTECTED BY 0.025 CM BRASS DISK		TABLE 2			336,000	7.5	-

*This table was prepared in cooperation with M. Visnov of Frankford Arsenal.

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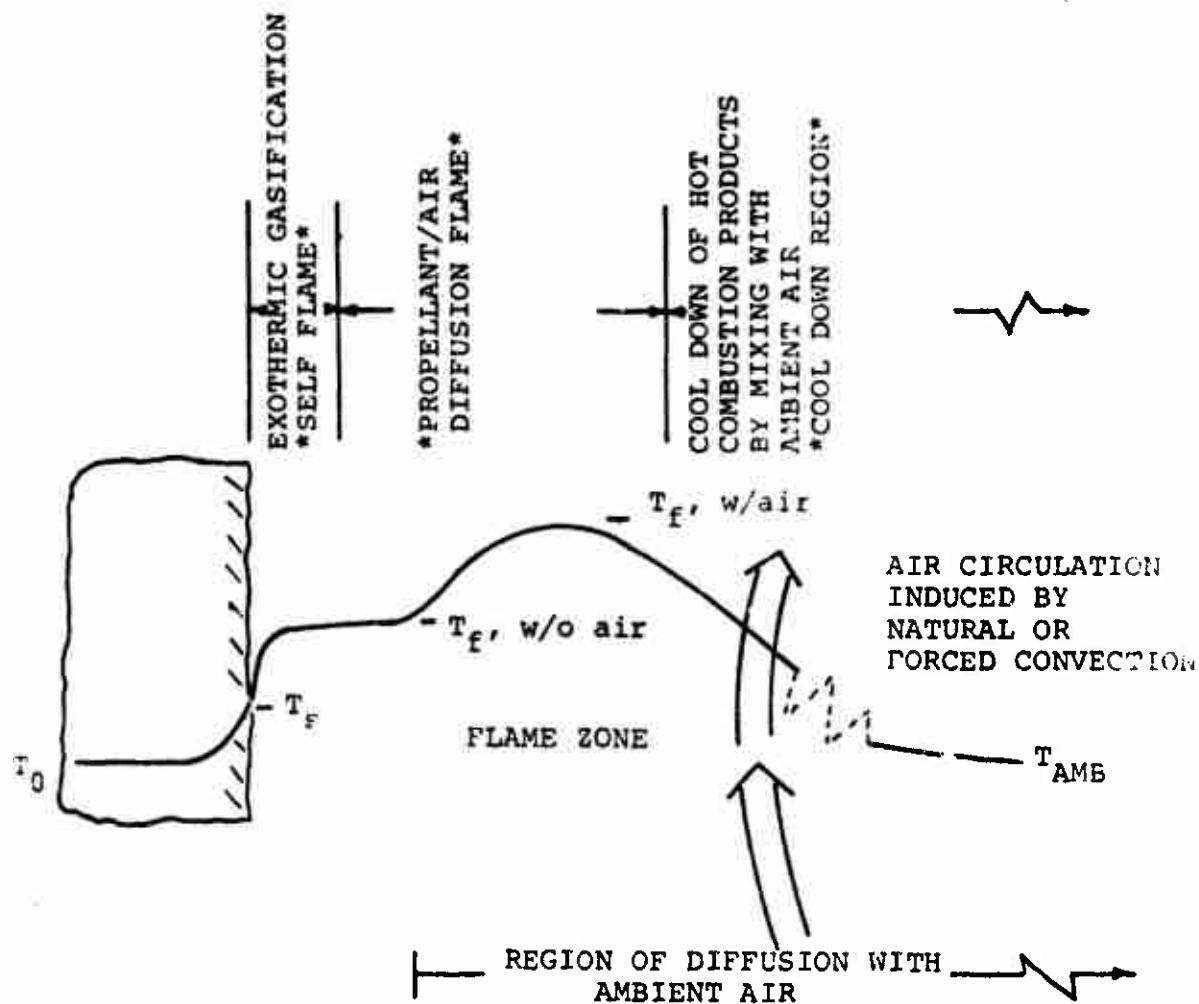
(a) Vigorous flame and correspondingly high surface blowing cause large separation between propellant surface and propellant products/air diffusion flame
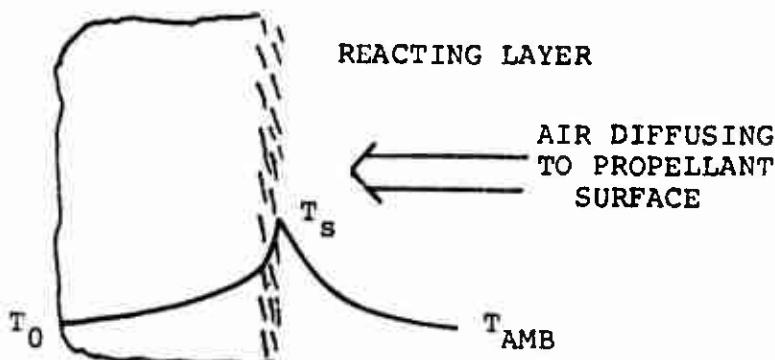
(b) Very slow burning (or smoldering) propellant and correspondingly low blowing permit O_2 to diffuse to and react on the surface.

Fig. 1 The processes which suppress propellant burning also increase the concentration of atmospheric O_2 at the reacting surface and thereby tend to defeat self-extingui ment.

PORTION OF OPERATIONAL
ENVIRONMENT IN WHICH
PROPELLANT WILL
SELF-EXTINGUISH
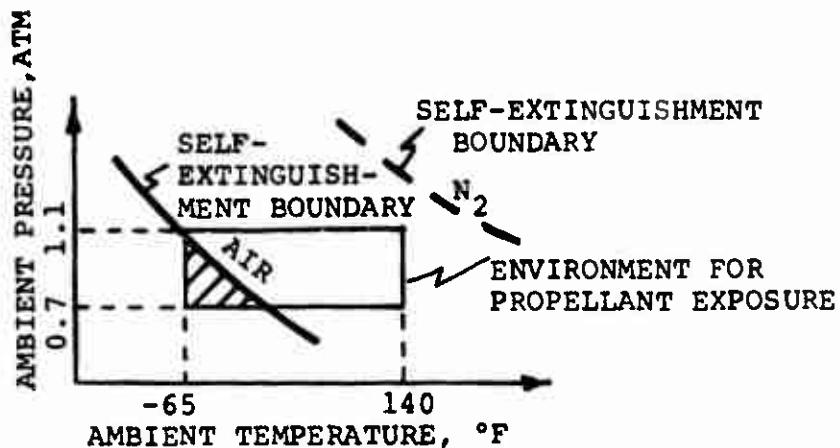
(a) Conventional propellant presents a flammability
hazard throughout most of its operational
environment.
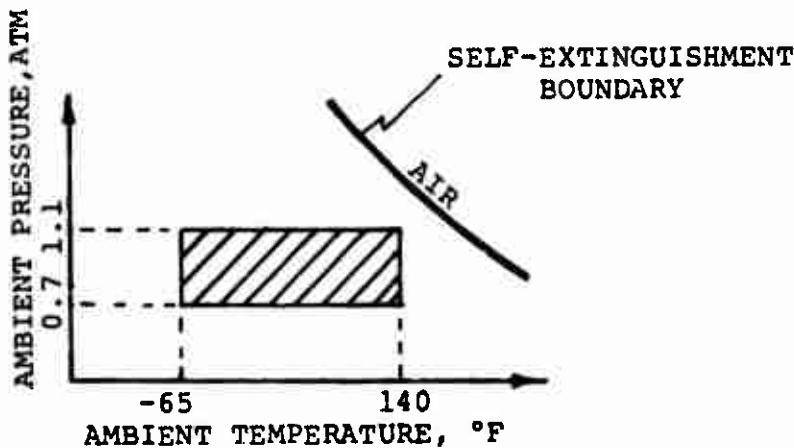
(b) Representation of the goal yet to be achieved, i.e.,
self-extinguishment boundary lies beyond environment
for propellant exposure.

Fig. 2 Illustration of the research goal of shifting the
boundary for self-extinguishment beyond the ambient
pressure and temperature range in which the propellant
will be exposed.

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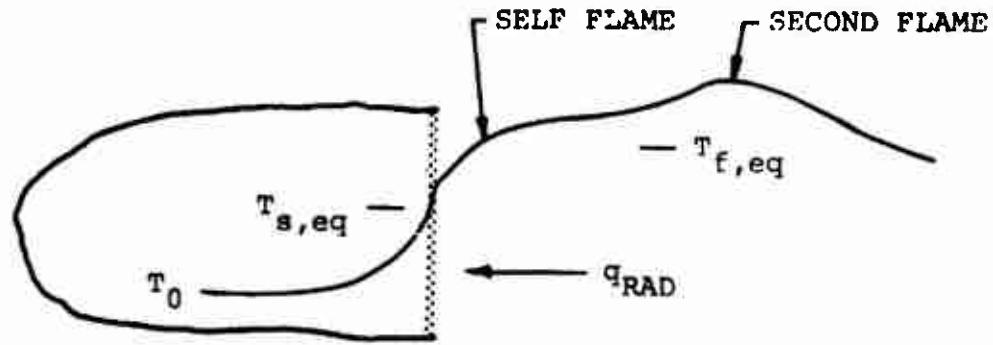
a) BURNING IS SUSTAINED BY IGNITION STIMULUS.
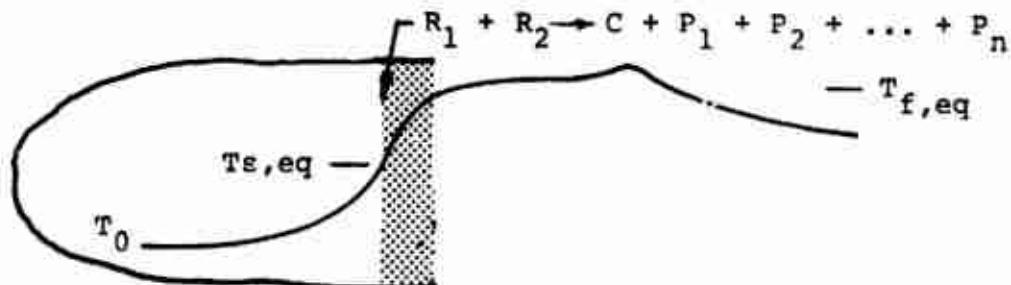
b) IGNITION STIMULUS IS REMOVED AND BURNING RATE ADJUSTS
AS FLAME INHIBITION "STRETCHES OUT" SELF-FLAME AND AS
CHAR INSULATES BURNING SURFACE FROM SECOND FLAME AND
FROM ATMOSPHERIC OXYGEN.
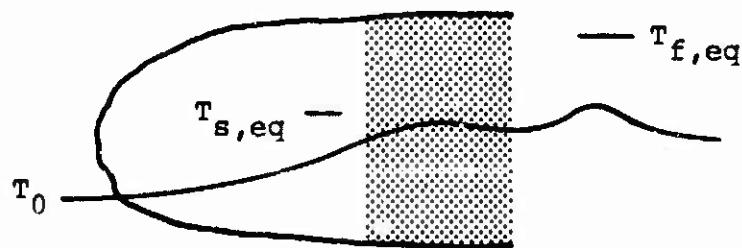
c) GAS EVOLUTION RATE HAS DECAYED SUFFICIENTLY THAT
HEAT FEEDBACK FROM GAS IS NOT SELF SUSTAINING.

Fig. 3 Failure to sustain combustion resulting from char
formation.
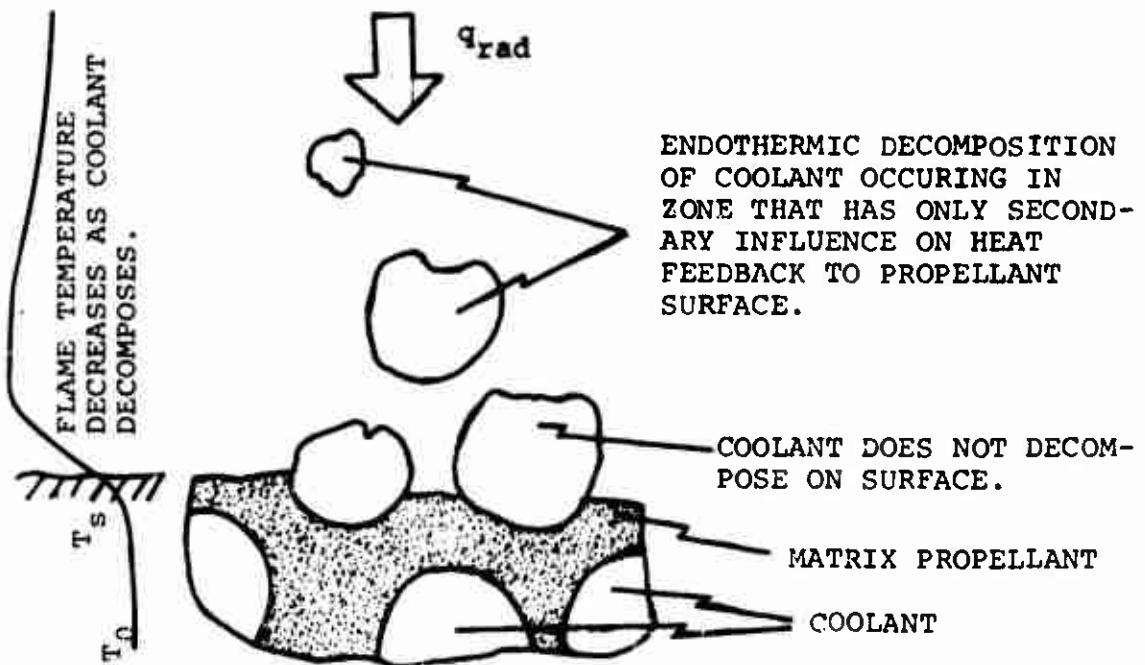
a) Coolant decomposition temperature higher than surface
   temperature of basic propellant. Thus the endothermic
   decomposition does not appreciably affect the zone
   that influences ignitability and burning rate.
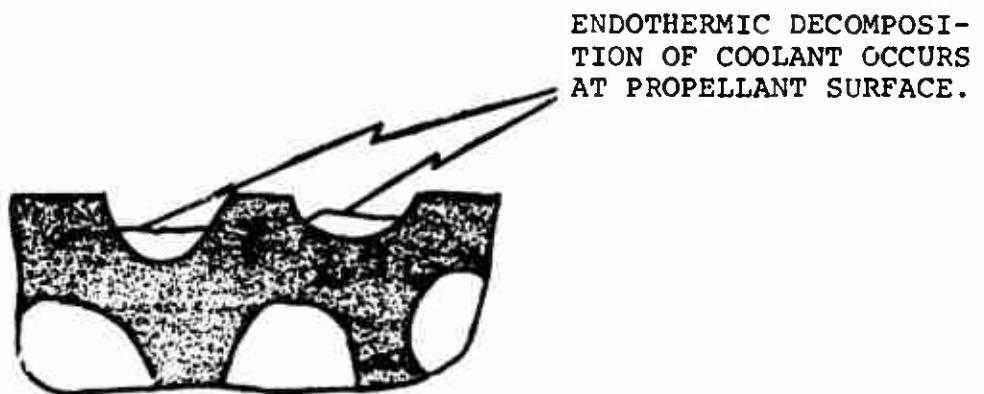
b) Coolant decomposition temperature is lower than the
   surface temperature. Thus, the endothermic decomposi-
   tion occurs in a zone where it has a profound influence
   on ignitability and burning rate.

Fig. 4   Conditions which determine whether a coolant will
          be effective in reducing propellant flammability.

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TEST EXPOSURE	CONTROLLED EXPERIMENT	
1. HOT GAS TORCH	T_g $\quad$ q/A U_g $\quad$ x_{O_2}	TORCH
2. HOT PLATE	T_{plate} $P_{CONTACT}$	PROP. PLATE
3. RADIATION	$\dot{q}/A$ U_{SWEEP}	RADIANT FLUX AIR
4. BURNING IN CONTROLLED ATMOSPHERE	p GAS	
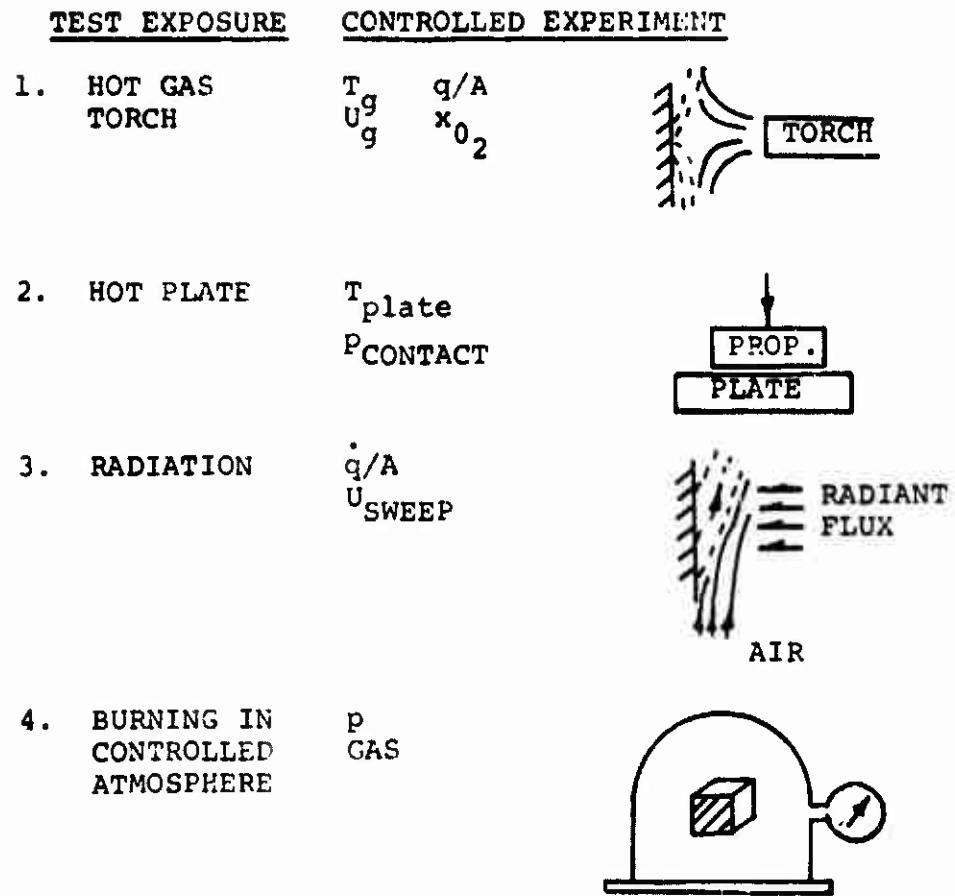
MEASURED:

TIME TO IGNITION,

$T(x,t)$ (IN SELECTED SAMPLES).

PRESSURE OF SELF-EXTINGUISHMENT.

BURNING RATE VERSUS AIR PRESSURE.

Fig. 5 Schematic representation illustrating the types of laboratory tests used to measure the effectiveness of flammability reducing modifications.
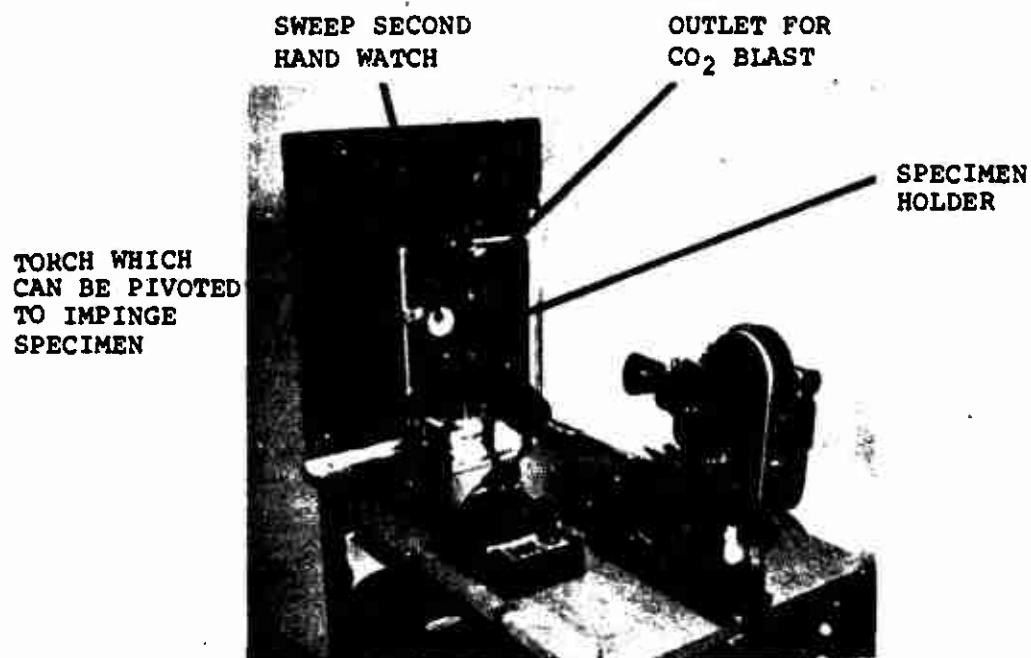
(a) Photograph of apparatus.
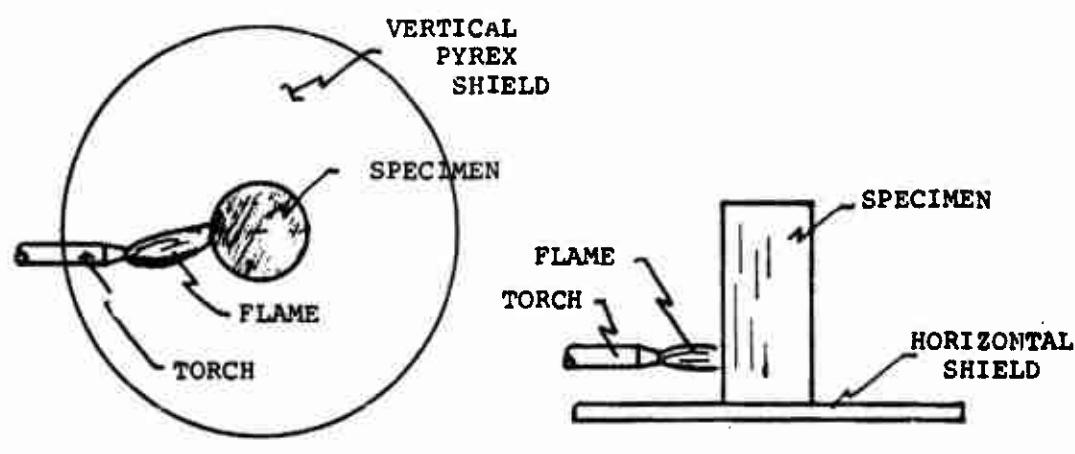
(b) Configuration for mounting and viewing horizontal specimen.

(c) Configuration for mounting and viewing vertical specimen.

Fig. 6 Apparatus to measure times and to photograph ignition and self-extinguishment processes that occur during and after exposure of propellant specimens to a calibrated flame.

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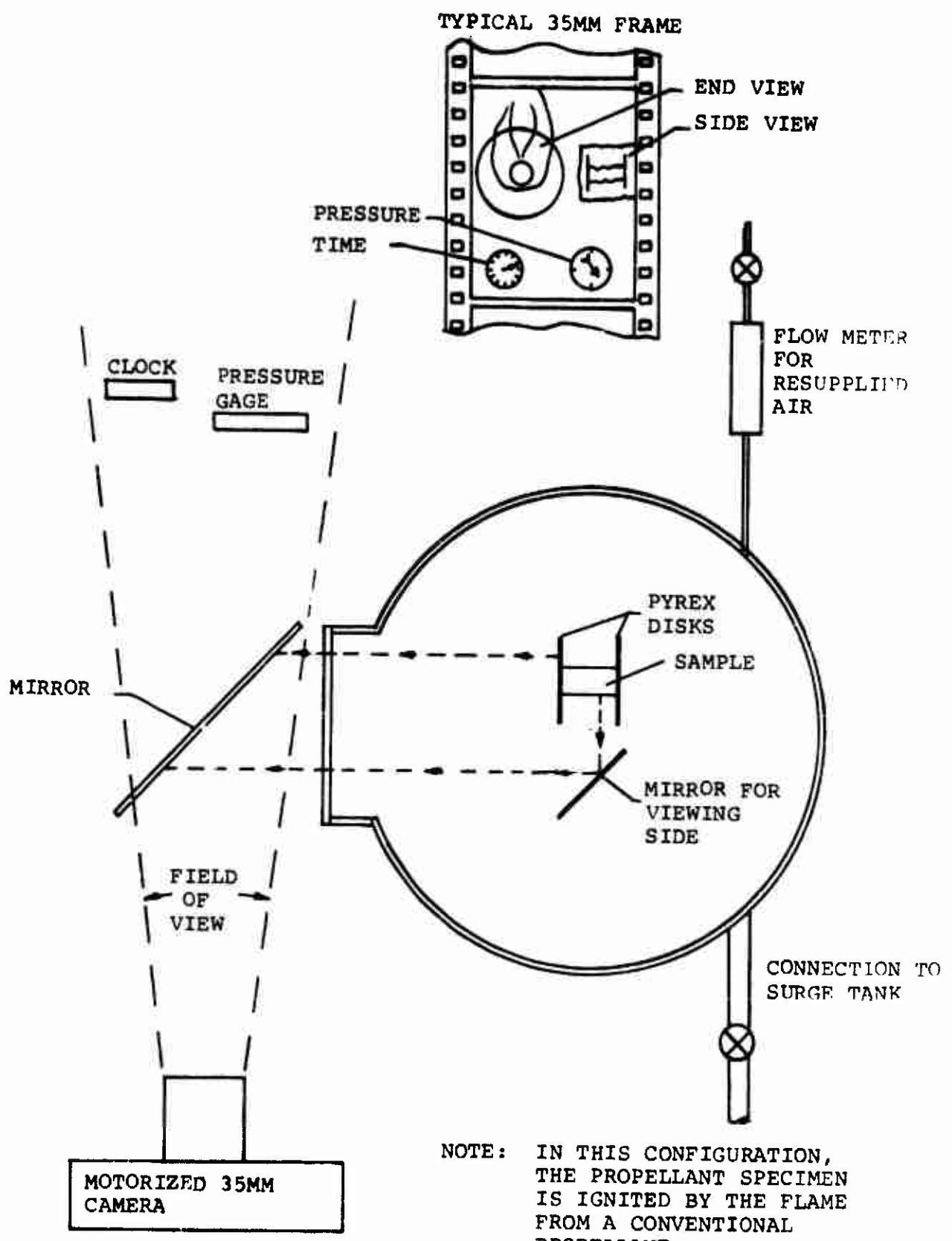
Fig. 7 Atmospheric chamber arranged for photographing
flame development and self-extinguishment.

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CONDITIONS:
AIR AT 1.0 ATM
PROPELLANT: CONTROL NC BASED
SIZE: 1.27 CM OD
        2.54 CM LONG

TIME, SEC.

12.7
11.7
10.7
8.5
7.4
6.4

VERTICAL
DIRECTION
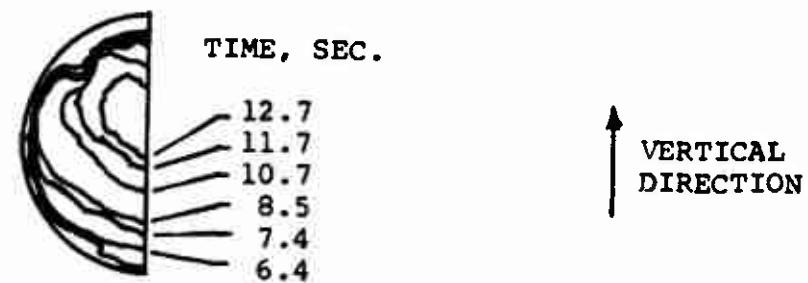
Fig. 8   Cross-sectional profiles of horizontal cylinder
         burning in air.

Fig. 9 Transient flame development around horizontal
cylinder burning in air.

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Fig. 10 Transient flame development around horizontal cylinder burning in air.

CONDITIONS:

AIR AT 1.0 TM
PROPELLANT: TCC/W-4 (10% OXAMIDE, 0.4%P)
SIZE: 1.27 CM OD
       2.54 CM LONG
COMBUSTION LEAVES RIGID ASH
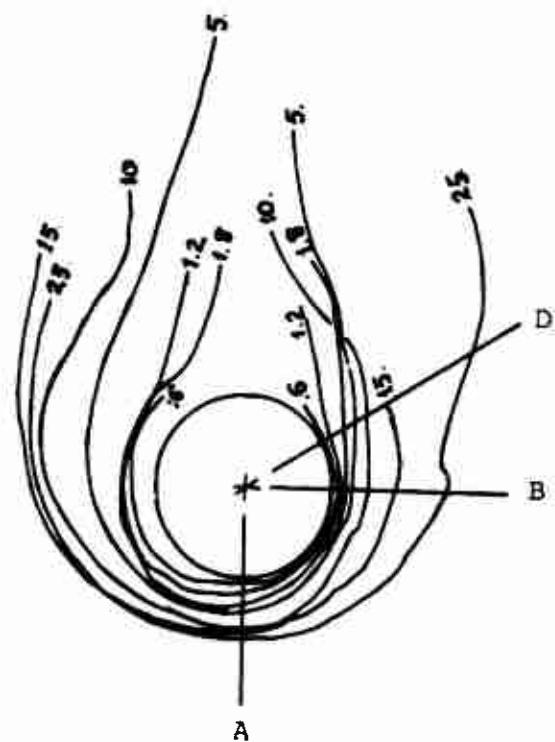
Fig. 11 Transient development of outer boundary of dark zone surrounding burning horizontal cylinder.

CONDITIONS:

AIR AT 1.0 ATM
PROPELLANT: TCC/W-5 (NO FLAME RETARDANTS)
SIZE: 1.27 CM OD
        2.54 CM LONG
COMBUSTION LEAVES RIGID ASH
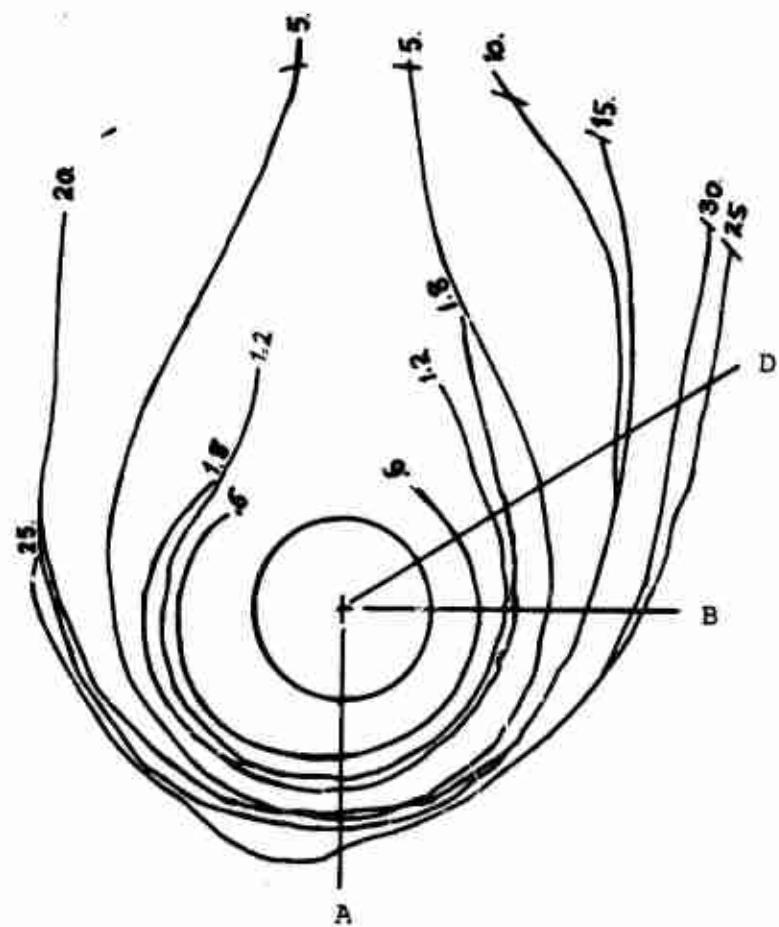
Fig. 12 Transient development of outer boundary of flame zone
        surrounding burning horizontal cylinder.
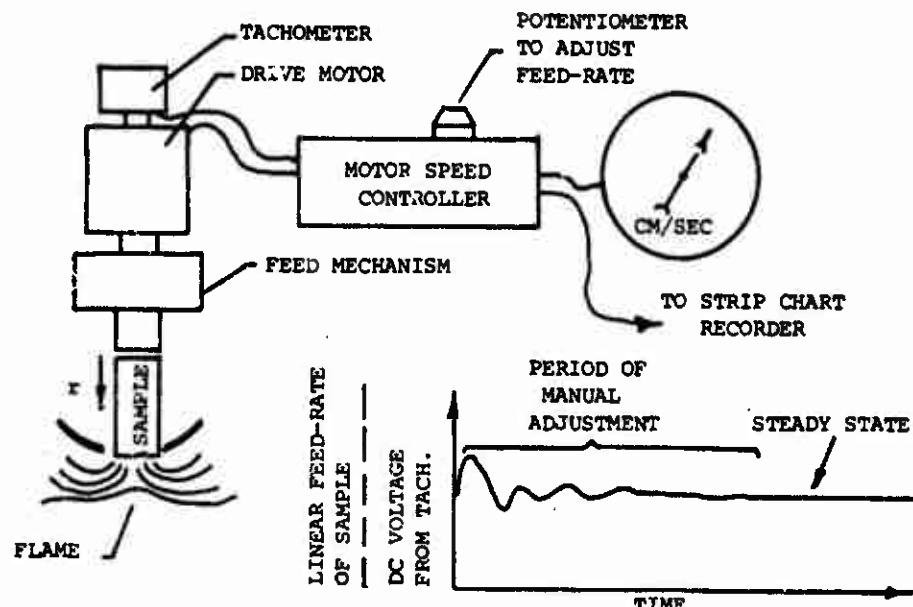
(a) Outline of procedure for controlling sample advancement so that it equals propellant burning rate.
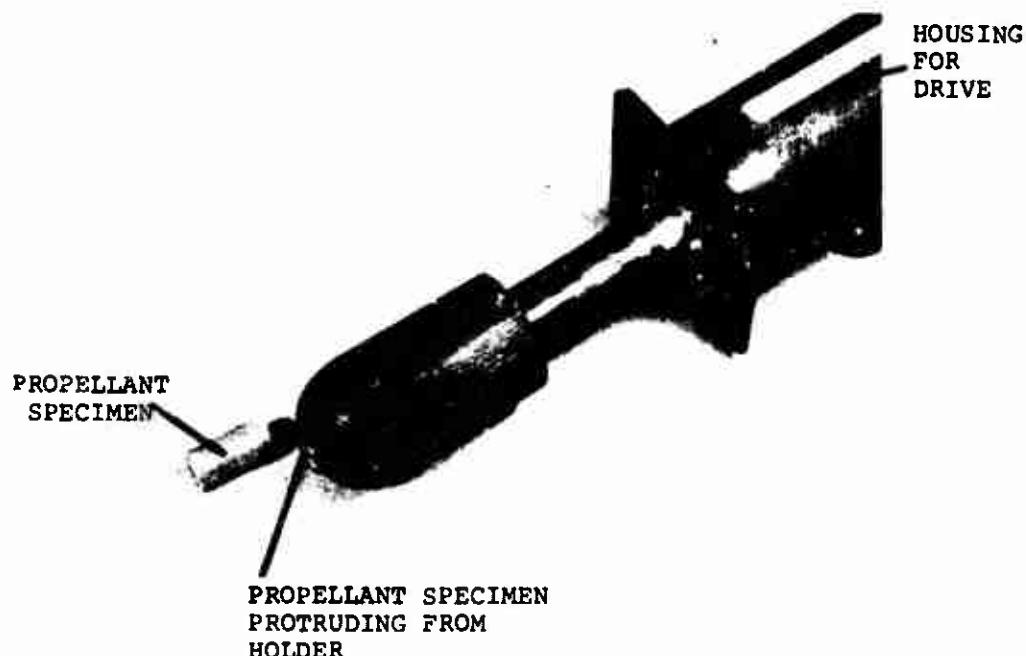
(b) Photograph of leading edge of specimen holder with specimen in place.

Fig. 13   Drive mechanism for advancing propellant to obtain steady state burning rates under ambient air conditions.
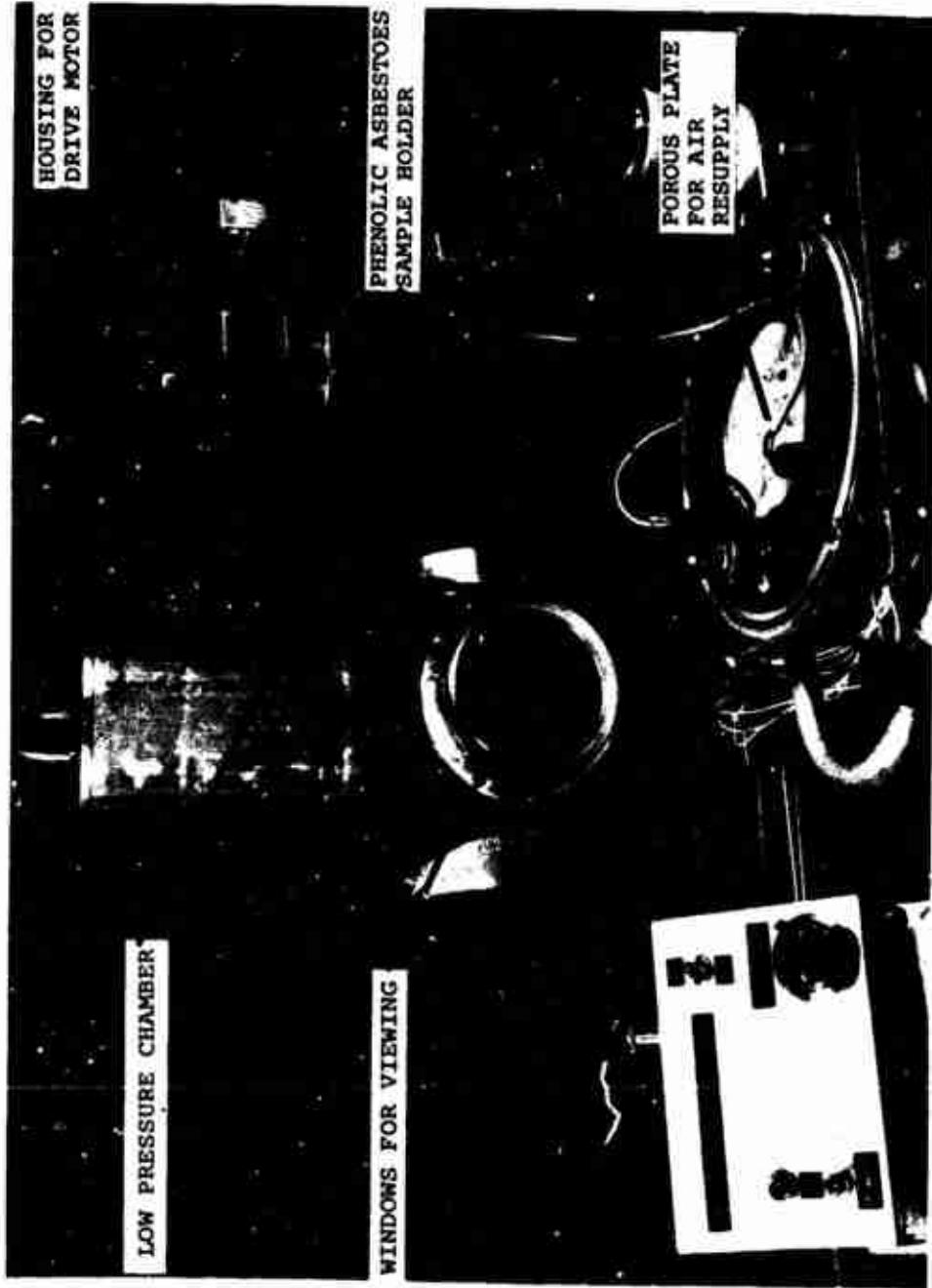
Fig. 14   Photograph of chamber for conducting experiments under controlled atmospheres (prototype for measuring steady state burning rates is in place).

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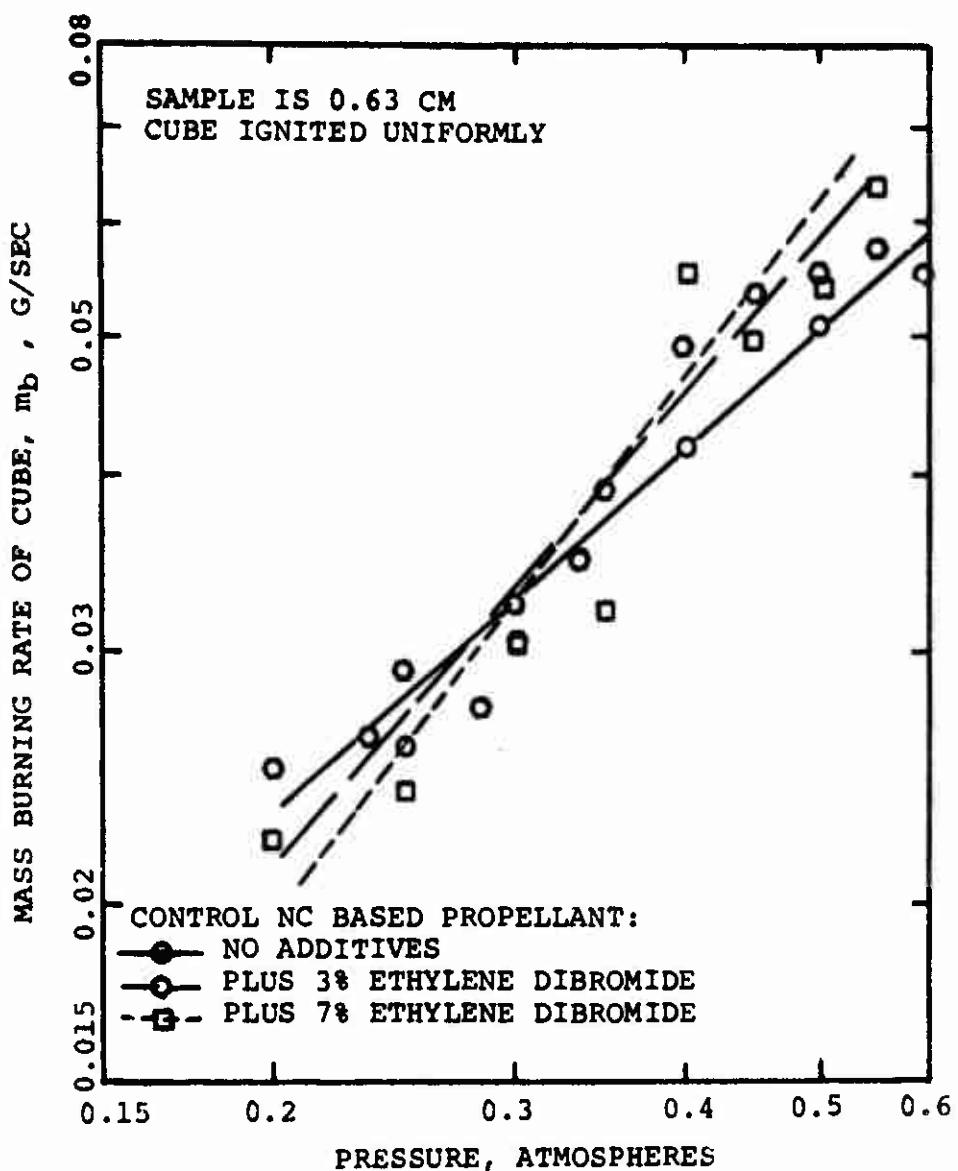
Fig. 15 Burning rate versus pressure of nitrocellulose
propellant modified with ethylene dibromide show-
ing that adding ethylene dibromide does not produce
a useful self-extinguishment point.
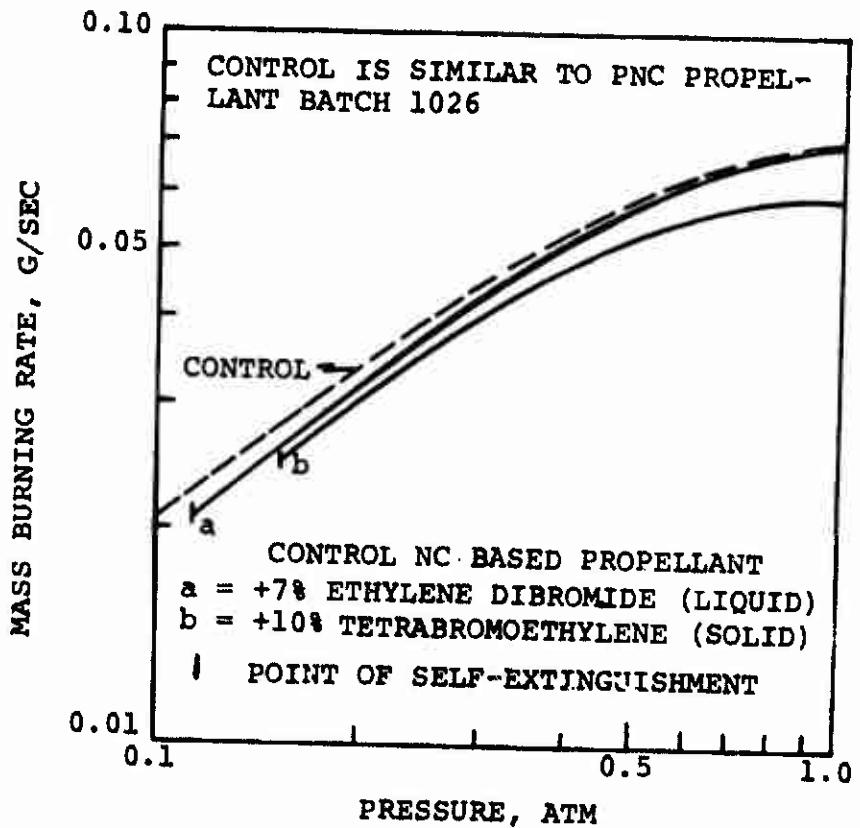
Fig. 16 Comparison of solid and liquid halogen
additives shows that neither are effective
flammability reducing agents.
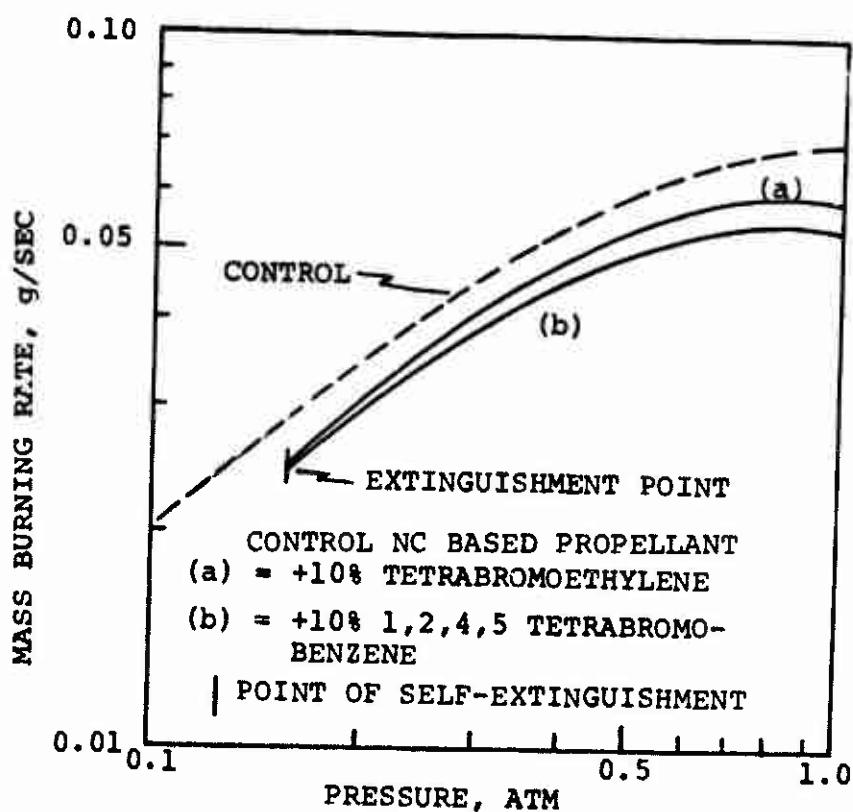
Fig. 17 Comparison of the effectiveness of a straight
chain (a) and ring (b) halogen shows that
neither are effective flammability reducing
additives.
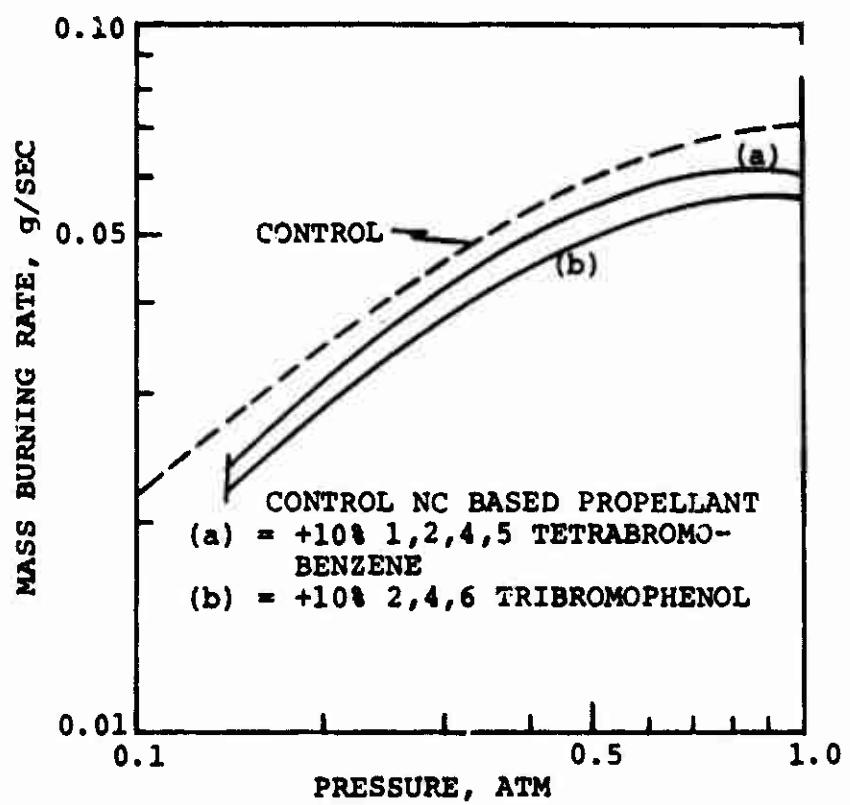
Fig. 18 Comparison of the effect of substituent
group (i.e., hydroxyl) on ring halogen
shows that modifying the ring halogen
is not effective in reducing flammability.
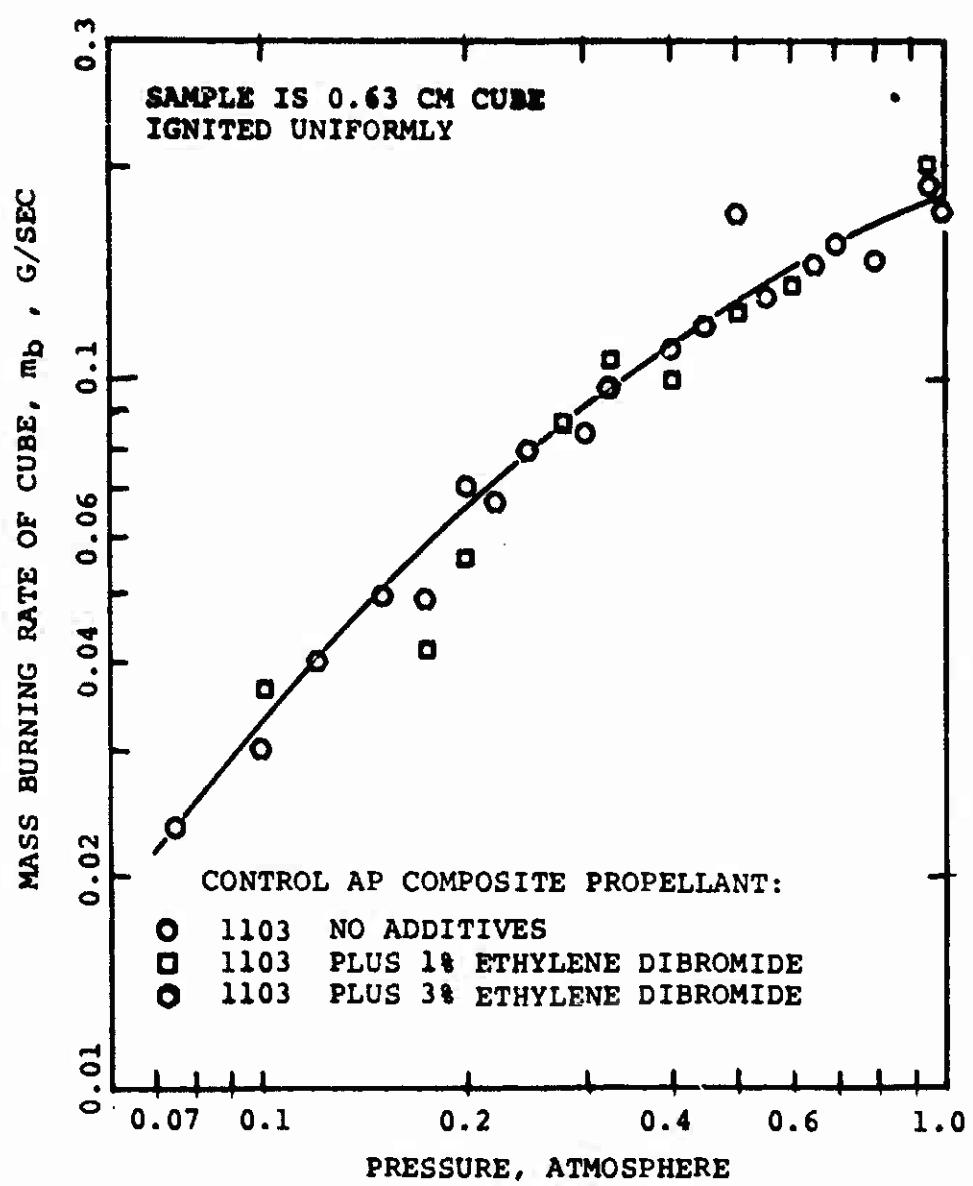
Fig. 19 Burning rate versus pressure of AP/PBAA composite propellant modified with ethylene dibromide showing that ethylene dibromide does not affect the burning rate characteristics in the low pressure range.
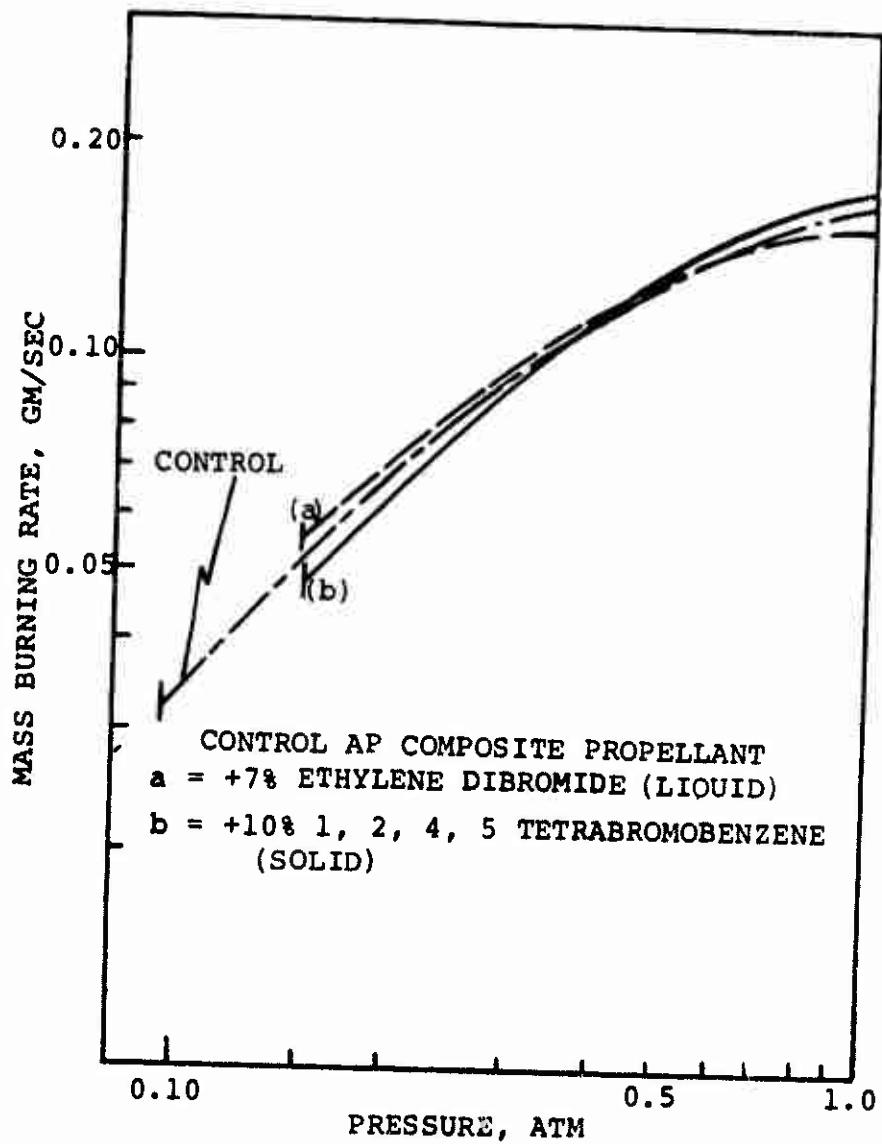
Fig. 20 Comparison of liquid and solid halogen
additives shows that neither is effective
flammability reducing agents in AP
composite propellants.
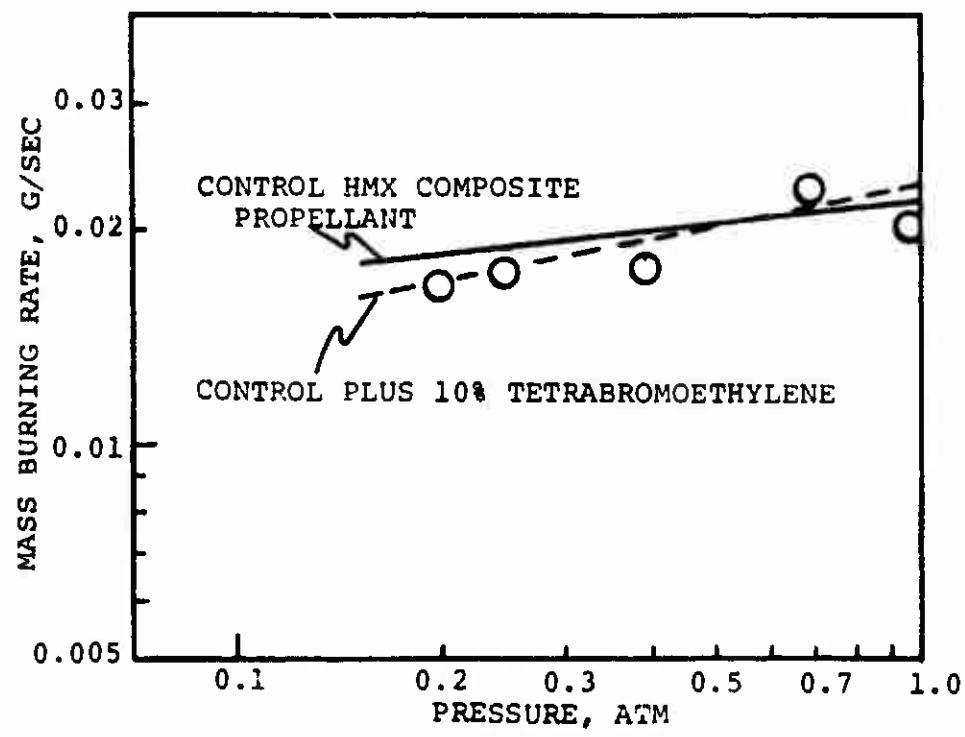
Fig. 21   Halogen additive does not modify mass burning
behavior and does not reduce flammability of
HMX Composite propellant.
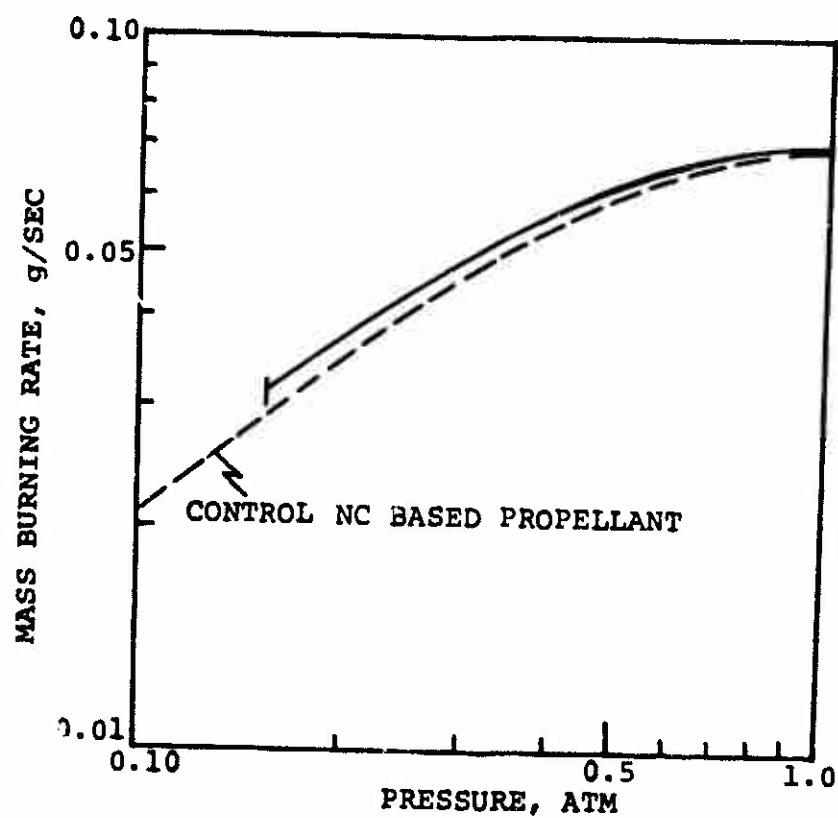
Fig. 22 5% phosphoric acid as an additive does
not reduce flammability.
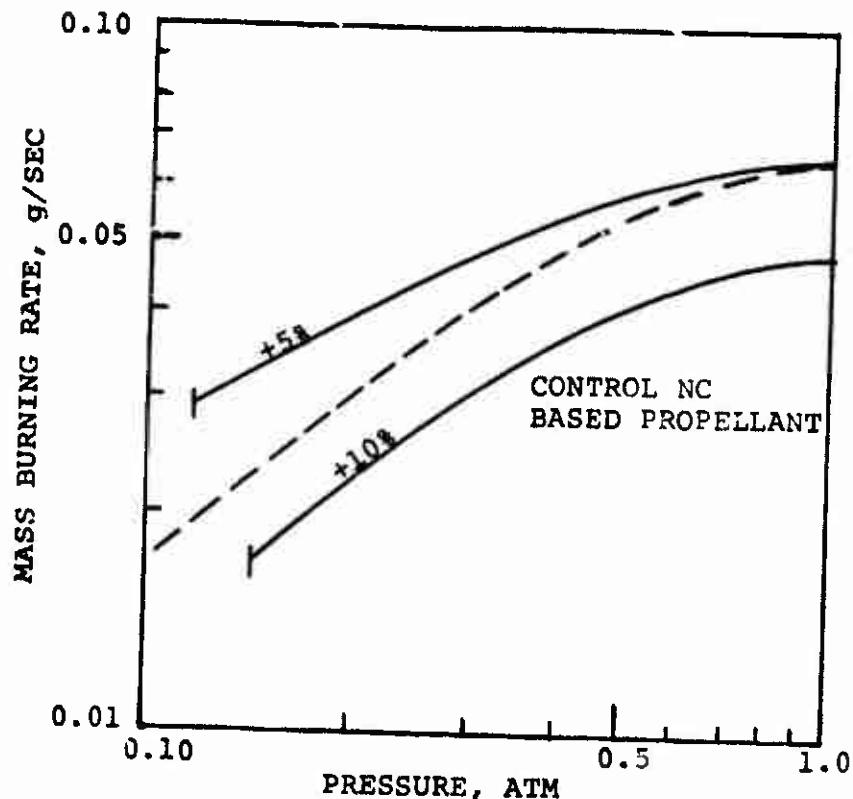
Fig. 23 5 and 10% ammonium phosphate
$[(NH_4)_2HPO_4]$ does not appreciably
improve flammability limit.
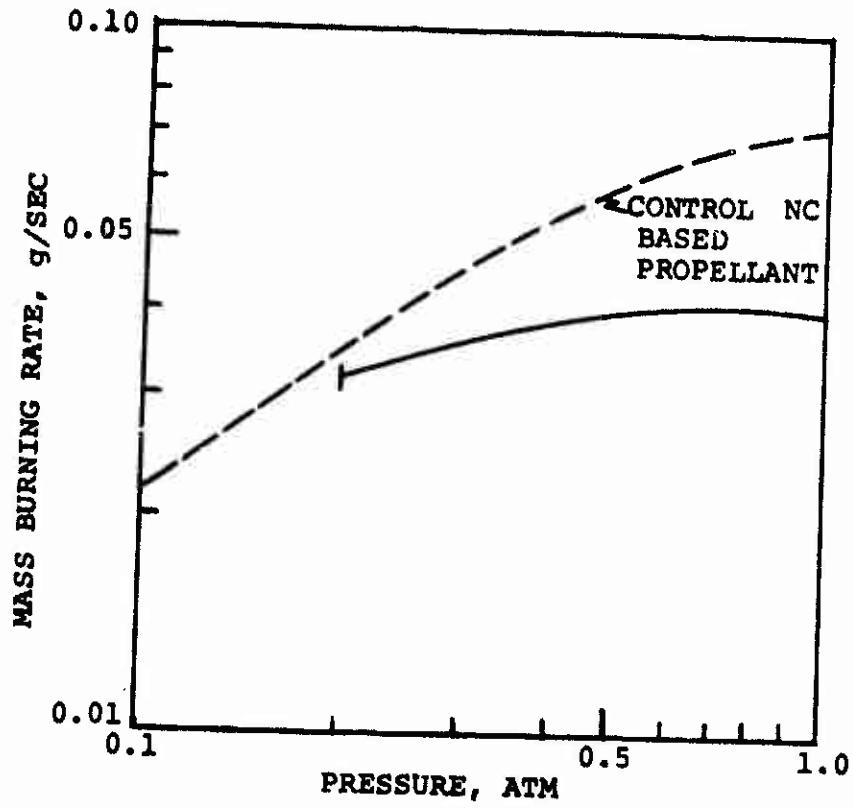
Fig. 24 10% triphenyl phosphate is not effective
in reducing flammability.
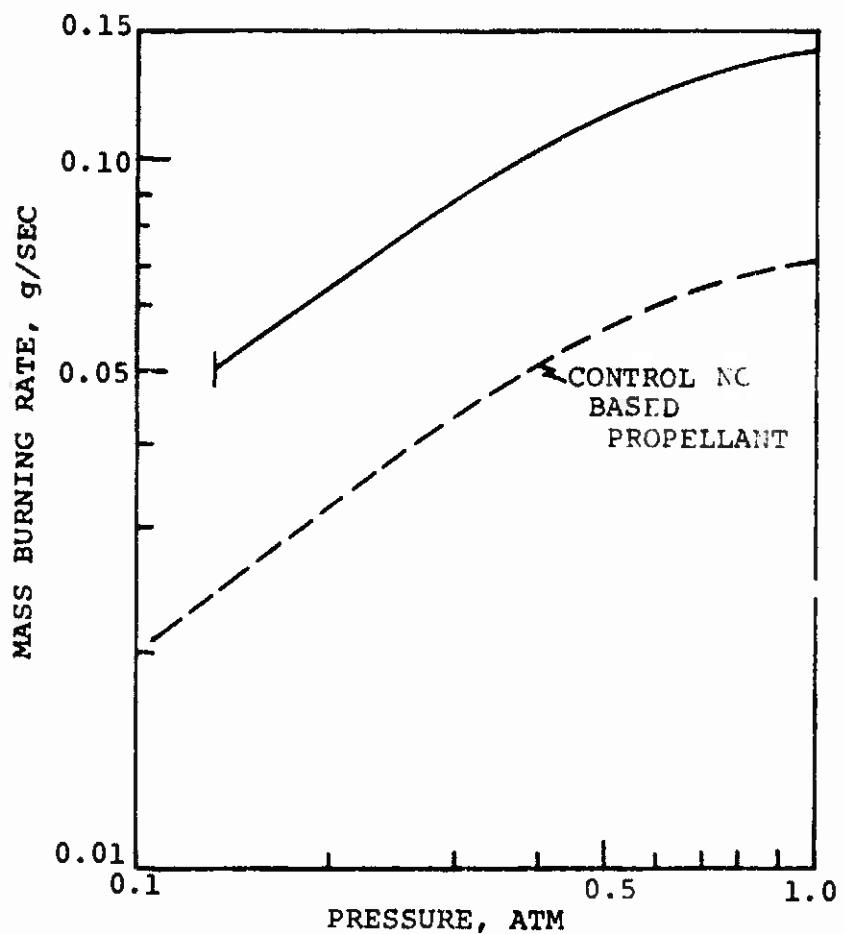
Fig. 25 10% triphenylphosphonium bromide as an
additive makes propellant more susceptible
to burning and does not reduce flammability.
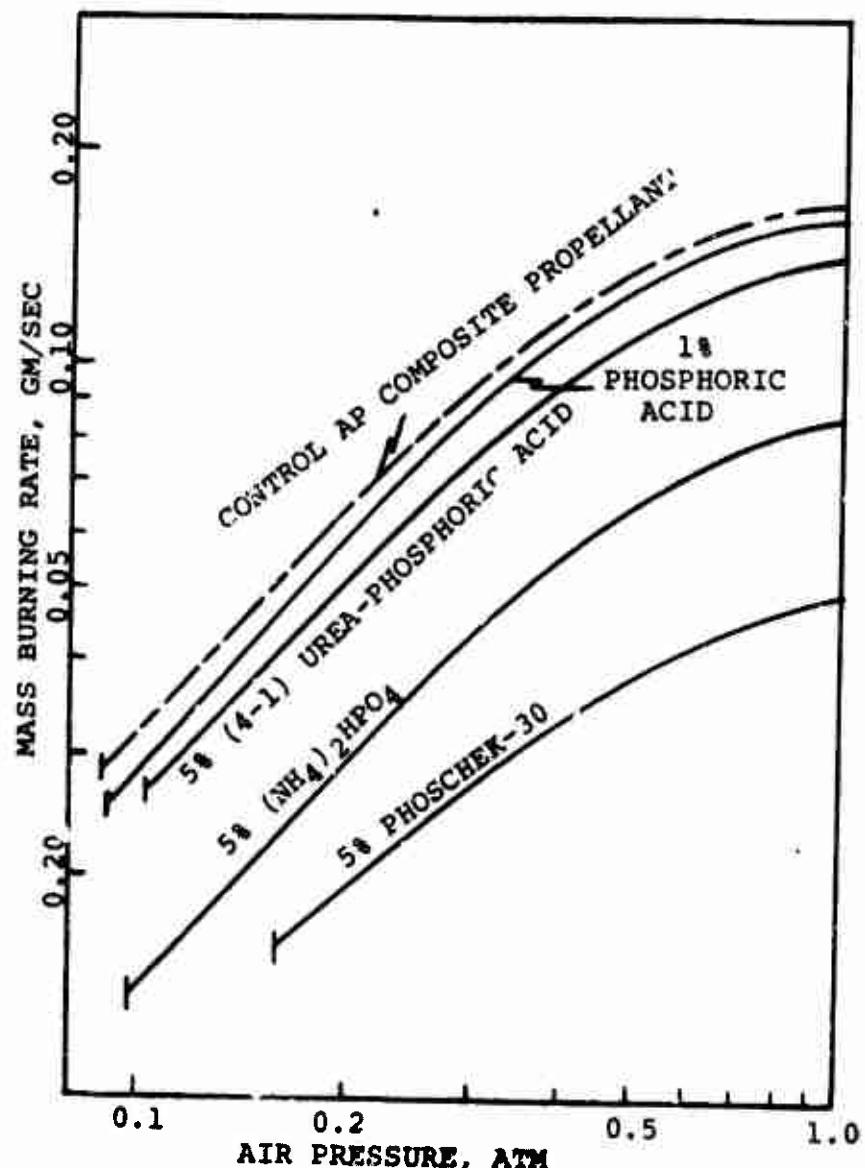
Fig. 26 Of the phosphorus containing compounds added
to AP composite propellants Phoschek 30 is
the most effective in reducing burning rate
but none of the additives produce an appre-
ciable reduction in flammability.
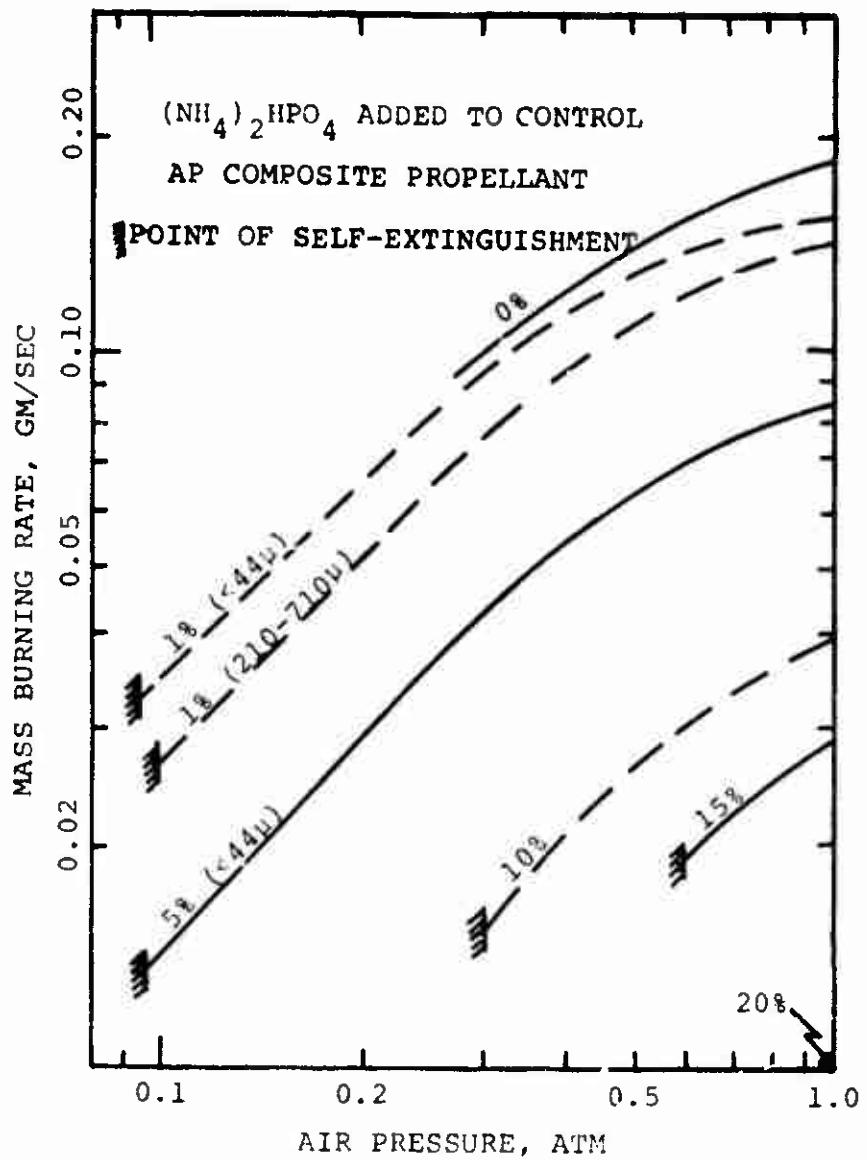
Fig. 27 Decrease of ignitability and burning
rate of AP composite with increased
phosphate loading.
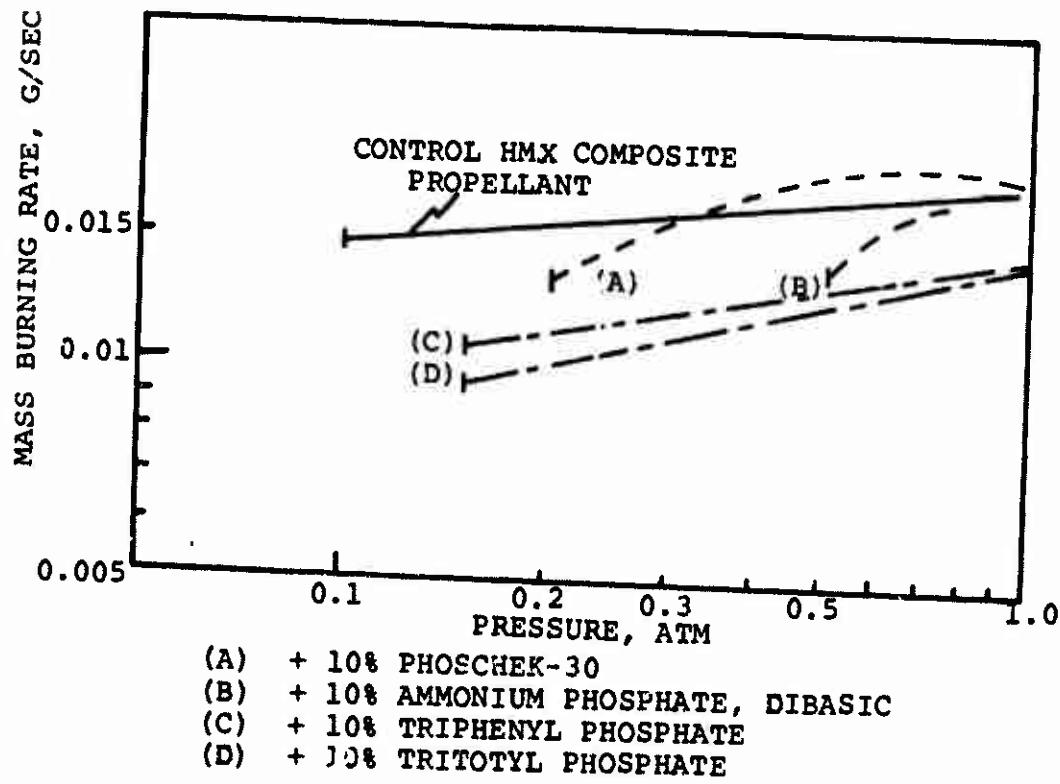
Fig. 28 Effect of phosphorus additives on HMX composite propellant mass burning rate and flammability limits.
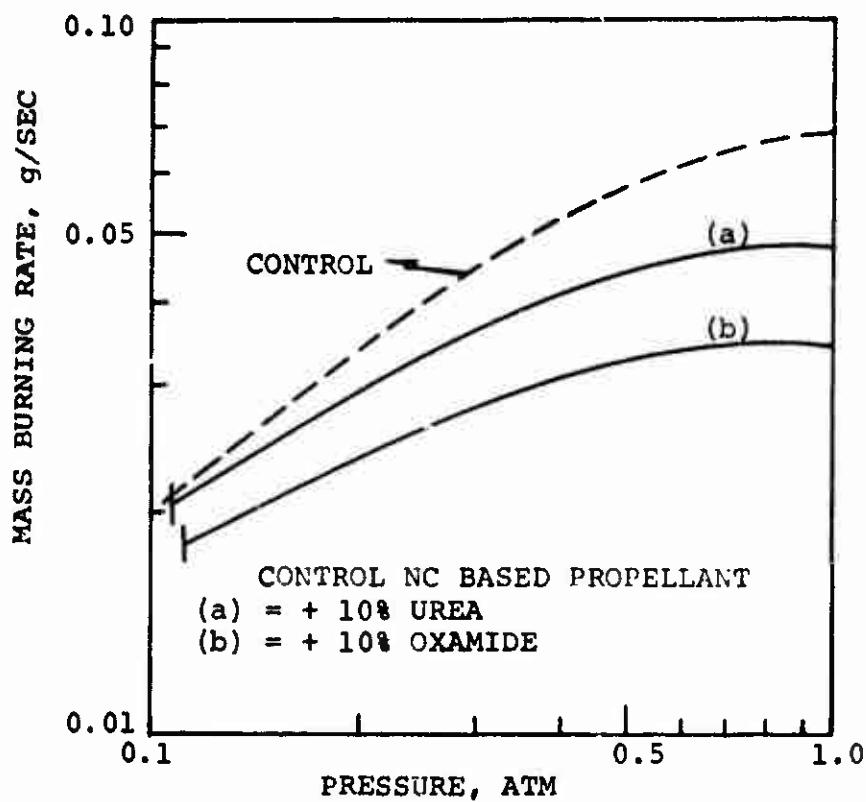
Fig. 29 Comparison of urea and oxamide as coolants
in reducing mass burning rate (not
effective in reducing flammability).
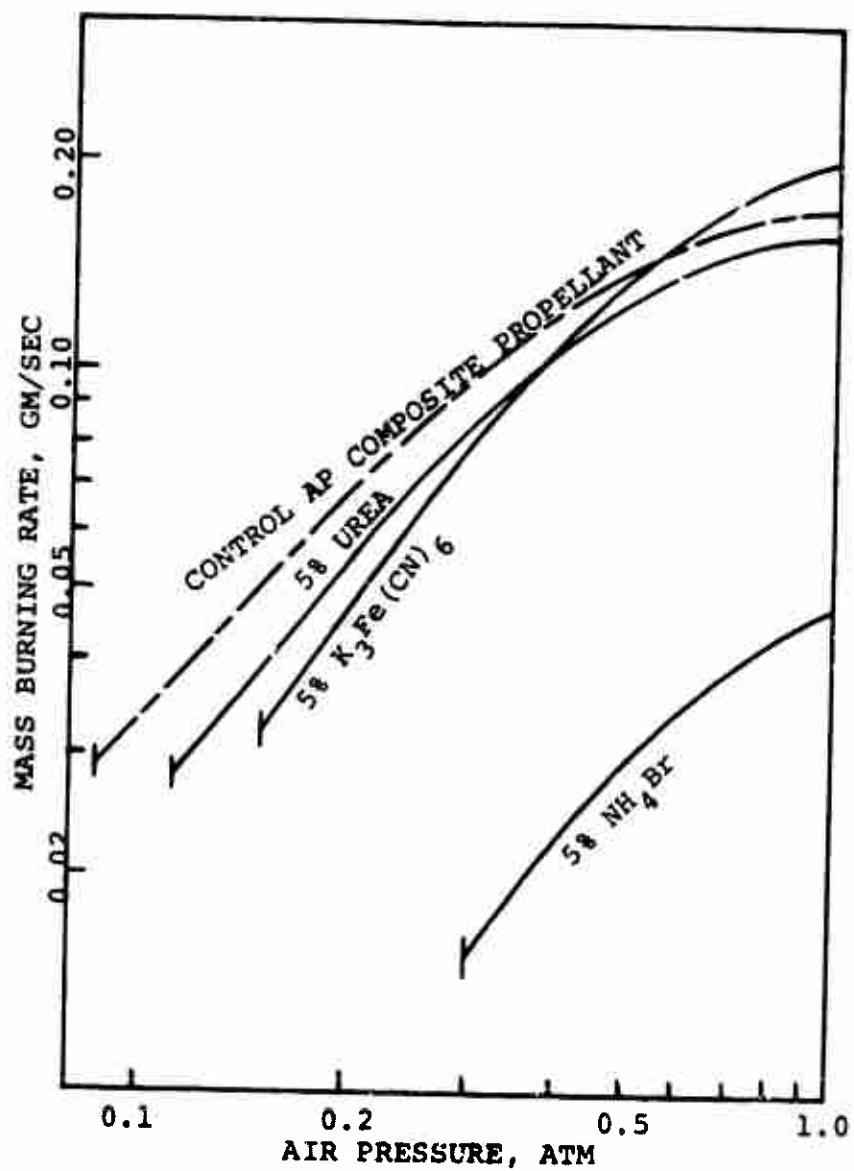
Fig. 30 Comparison of coolants used in AP composite
propellants shows that NH4Br is the most
effective in decreasing flammability and
greatly reduces burning rate.
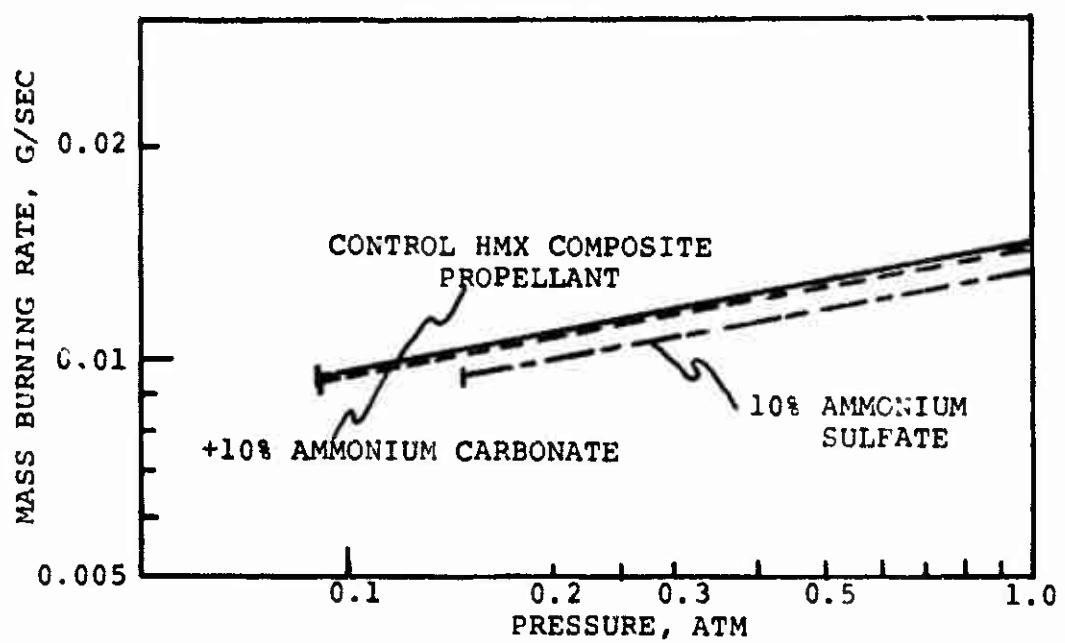
Fig. 31 Coolants in HMX composite propellant produce no
significant flammability reduction or modification
of mass burning rate.
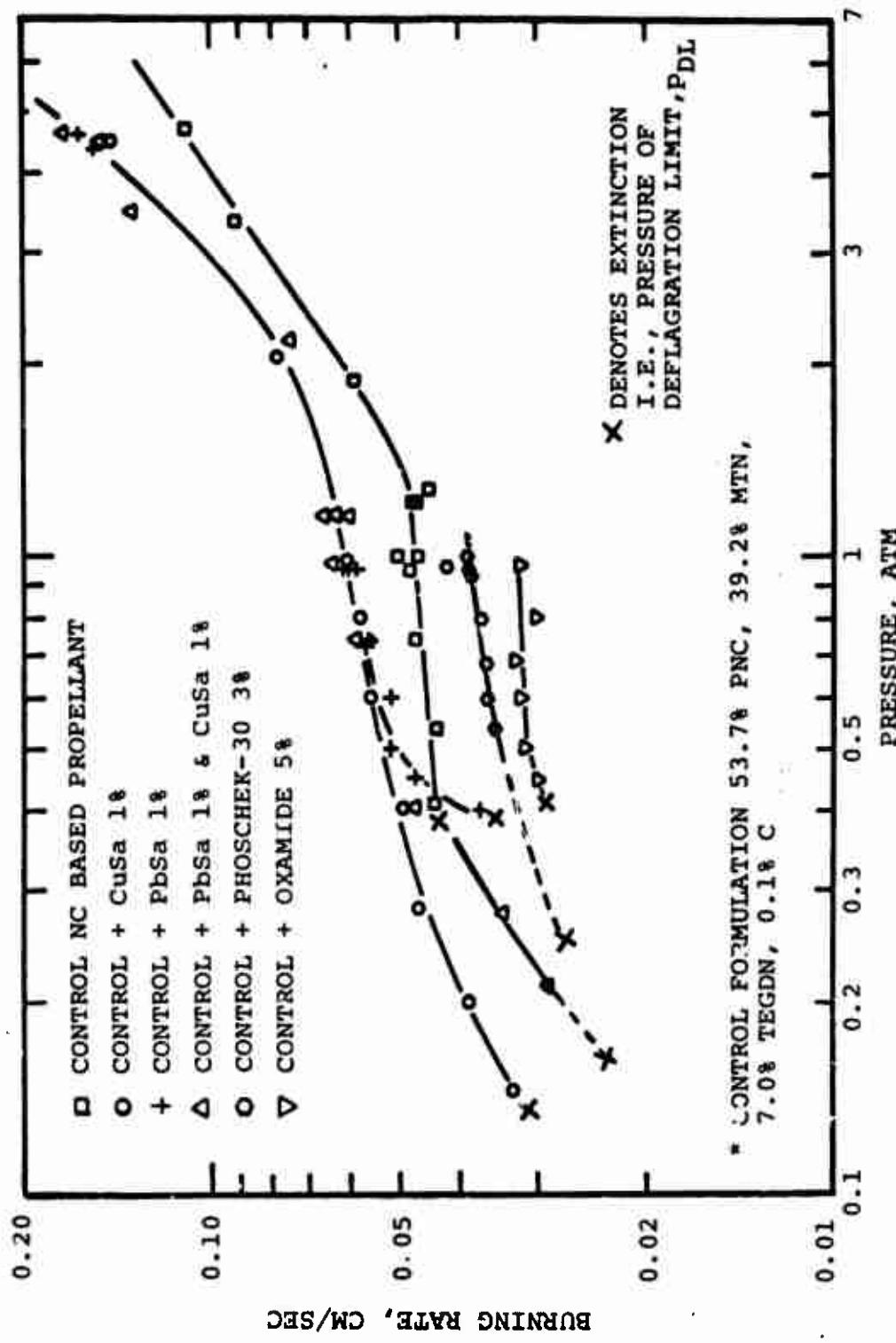
Fig. 32   Effect of additives on burning rate and pressure of deflagration limit in N_2 showing that oxamide reduces burning rate by 20%.
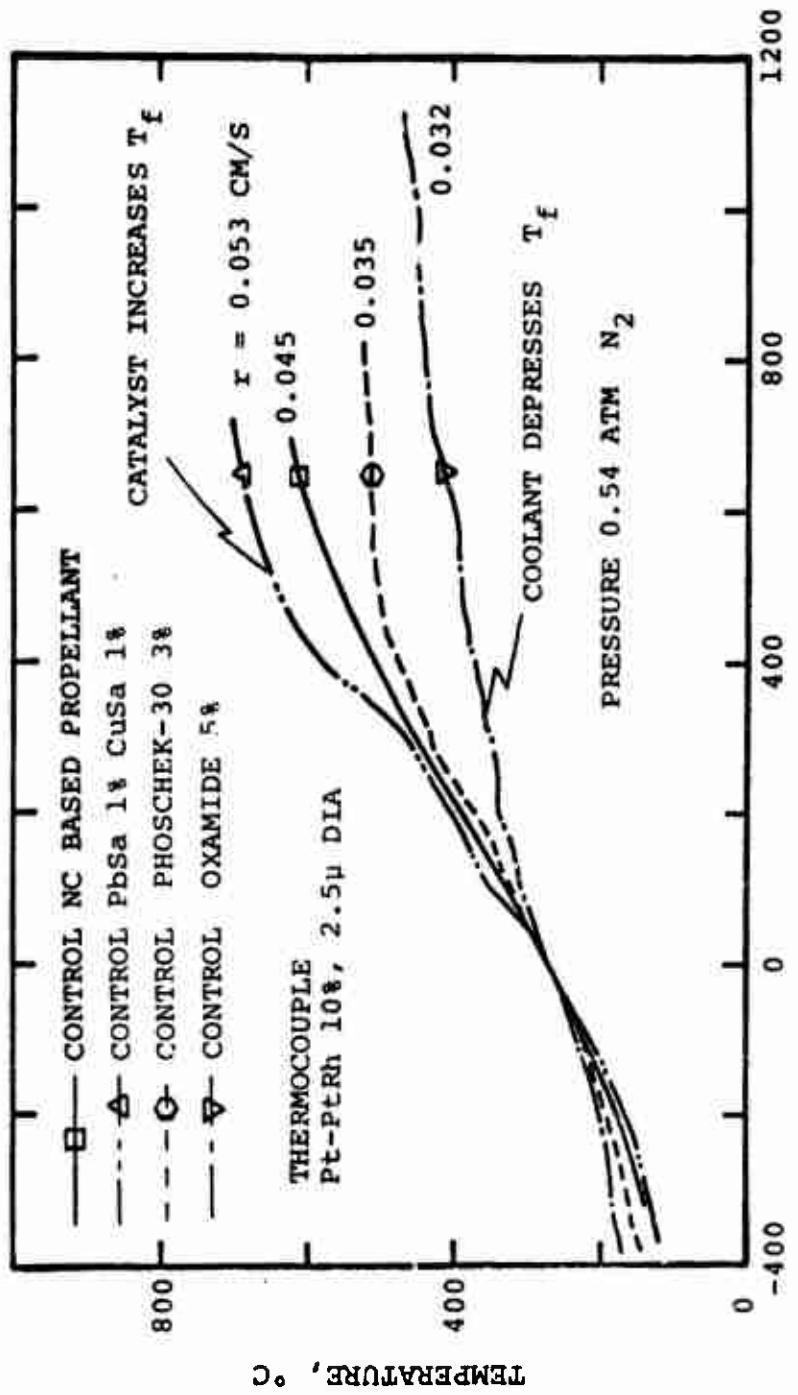
Figure 33   Measured temperature vs distance in condensed phase and flame
zone showing how flammability retarding additives reduce
temperature gradients and flame zone temperatures.
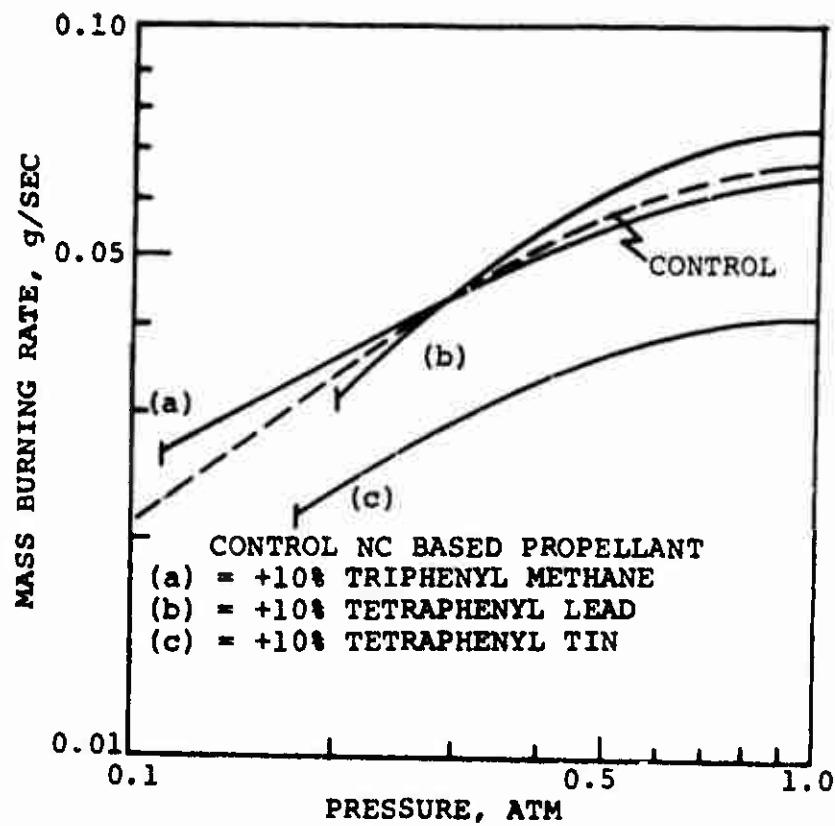
Fig. 34 Comparison of tetraphenyl compounds showing
that they are not effective in reducing the
flammability of nitrocellulose propellants.
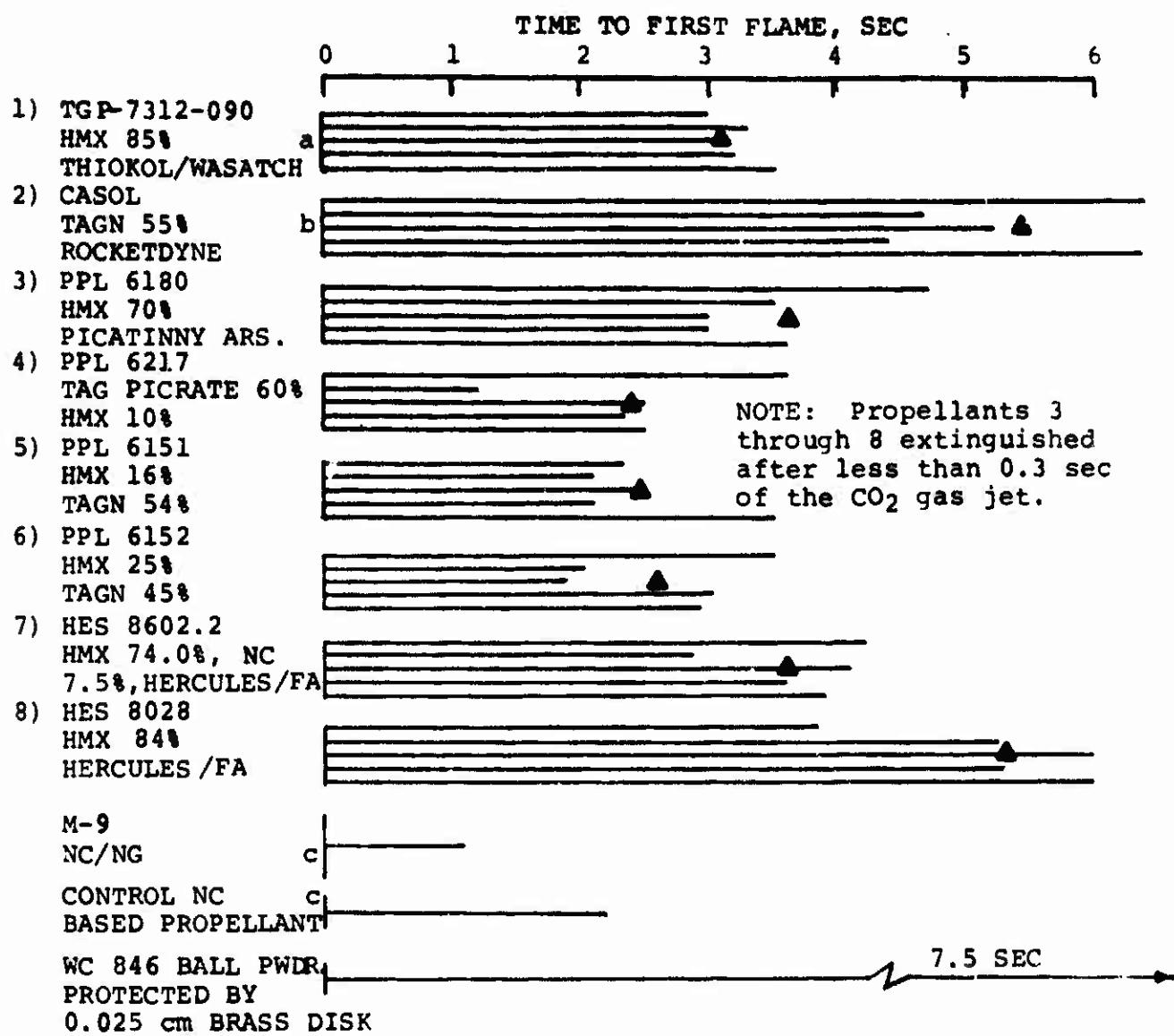
Fig. 35 Times to ignition of propellants provided by Frankford
Arsenal (propellant compositions summarized in Table 8).

a) Steady State Conditions

b) Depth of preheat

Slow heat-up-to-ignition

Fast heat-up-to-ignition

c) Example of deep preheat region resulting from low heating rate

Surface

Preheat Zone corresponding to steady state burning

Zone heated during slow heat-up-to-ignition

Preheated region which is more likely to retain flame
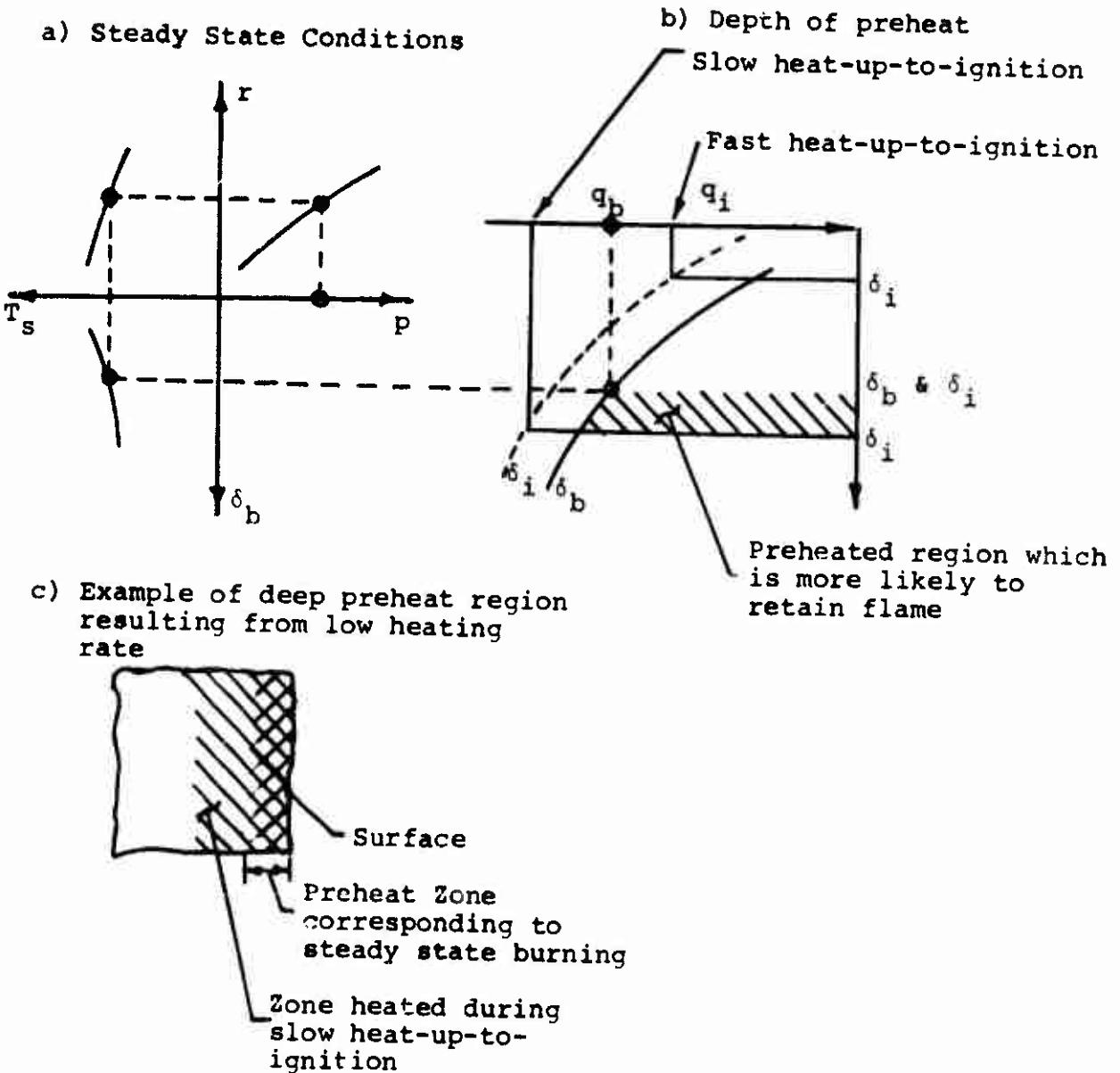
Fig. 36 Effect of low heating rate on conditions for self-extinguishment

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